

ANALYSIS OF SOIL LEAD LEVELS IN AN HISTORIC DISTRICT OF A SOUTH
CENTRAL KENTUCKY CITY

A Thesis

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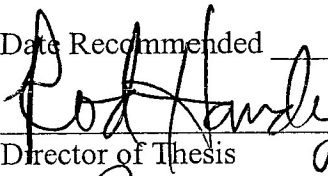
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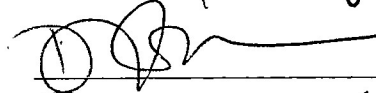
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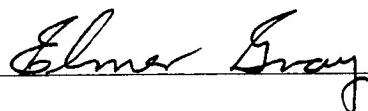
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ANALYSIS OF SOIL LEAD LEVELS IN A HISTORIC DISTRICT OF A SOUTH
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TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	iii
LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
ABSTRACT.....	viii
CHAPTER 1: INTRODUCTION.....	1
CHAPTER 2: LITERATURE REVIEW.....	7
CHAPTER 3: METHODS.....	21
CHAPTER 4: RESULTS.....	26
CHAPTER 5: DISCUSSION.....	32
LIST OF REFERENCES.....	38
APPENDIX	
A Soil Lead Sampling Permission Agreement.....	43
B EPA Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.....	45
C Year of Construction and Soil Lead Levels for Samples.....	69

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Percentage of Housing Units with Higher Soil Lead Levels by Age of Construction.....	13
2 Percentage of Housing Units with Deteriorating Paint by Age of Construction.....	15
3 Characteristics of Sample.....	27
4 Geometric Means Soil Lead Levels	28
5 One-Way ANOVAs for Soil Lead Levels by Exterior Composition ..	31
6 t-Test Analysis of Soil Lead Levels by Fully Painted and Non-Painted Housing Units.....	31

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Lead-Based Paint as a Direct and Indirect Source of Lead Exposure in Children.....	3
2 Decline in Blood Lead Action Levels.....	7
3 Estimated Number of Children with Blood Lead Levels > 10 μ g/d.....	9
4 Geometric Mean Blood Lead Levels in Children Ages 1-5.....	9
5 Geometric Mean Soil Lead Levels by Exterior	28
6 Geometric Mean Soil Lead Levels by Paint Loading	29
7 Geometric Mean Soil Lead Levels by Age	29

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Lead in soil has been shown to be a significant pathway of lead exposure in children. Several factors including age of housing units, exterior composition, and paint loading may affect the amount of lead present in the soil. The purpose of this study was to analyze soil lead levels on properties located in an historic district and relate those levels to the variables previously mentioned. A total of 30 soil samples were collected from housing units in a nationally recognized historic district. Concentrations of lead in the soil were analyzed using a NITON X-ray Fluorescence Spectrum Analyzer, following EPA Method 6200 and the instrument protocol. Significant differences were found between the soil lead levels and paint loading (fully painted vs. non-painted). Significant differences were also found between soil lead levels and exterior surface (frame, brick, and other). A correlation analysis revealed there was no correlation between housing age and soil lead levels.

Soil lead can be used as a predictor of blood lead levels in children. Using the information regarding soil lead concentration, the relative risk of exposure to lead and the subsequent health effects can be estimated for children living in the study area. The

results from this study can also be used to initiate other studies and develop educational strategies for the district.

CHAPTER 1

INTRODUCTION

“The problem is so well defined, so neatly packaged with both causes and cures known, that if we do not eliminate this societal crime, our society deserves all the disasters that have been forecast for it”—Rene Dubos on lead (City of St. Louis, 1997).

The association between lead-based paint and childhood lead poisoning was first documented as early as 1904 when Australian doctors linked lead poisoning cases to paint on walls and verandas (“History of Lead Advertising,” 2003). One of the first documented cases of lead poisoning in the United States was in 1914 at which time a boy died from lead poisoning after ingesting paint from the railings of his crib (“History of Lead Advertising,” 2003). During the 1970s, health officials in the United States described childhood lead poisoning as a “silent epidemic.” Despite these early warnings, an estimated 434,000 children in the United States still had elevated blood lead levels between the years 1990 and 2000 (“Children’s Blood Lead Levels,” 2003).

Acute effects from high concentrations of lead in children include permanent neurological damage, lead colic, coma, and death (Muir & Campbell, 1995). More common though are the chronic health effects from lower levels of lead: impaired cognitive development, decreased intelligence, learning disabilities, behavioral problems, (Lead Based Paint and Hazard Reduction and Financing Task Force, 1995), and anemia (Muir & Campbell, 1995).

Lead-based paint is believed to be the primary contributor to lead exposure in children (Xintaras, 1992). However, H.W. Mielke, Anderson, et al. (1983) concluded, “about 40 to 45 percent of the confirmed lead toxicity cases in the U.S. could not be directly related to lead paint” (p. 1366). The conclusion: lead-contaminated soil and dust are significant contributors to lead exposure (H.W. Mielke, Anderson, et al., 1983). Today, lead-based paint, lead-contaminated soil, and dust remain the three primary sources of lead exposure (H.W. Mielke, Anderson, et al., 1983; Rosen & Munter, 1994).

As depicted in Figure 1, lead-based paint is both a direct and indirect source of lead exposure in children (Charney, Sayre, & Coulter, 1980). Though lead-based paint is the most widespread of all the sources (Xintaras, 1992), soil and dust represent the most significant routes of lead exposure in children (Muir & Campbell, 1995). Direct exposure to lead results from the ingestion of paint chips (Jacobs et al., 2002). Children are indirectly exposed to lead through contaminated soil and dust. As exterior paint deteriorates, lead is deposited into the soil. Children playing in the soil may inadvertently ingest lead particles through hand-to-mouth contact (Xintaras, 1992; Jacobs et al., 2002). Dust may become contaminated with lead as interior painted surfaces are disturbed (e.g., brushed or chipped) or as contaminated soil is carried indoors (Charney et al., 1980). These dust particles may be inhaled or ingested as dust is deposited onto objects that may later come into contact with a child’s mouth (United States Environmental Protection Agency [EPA], 2001a).

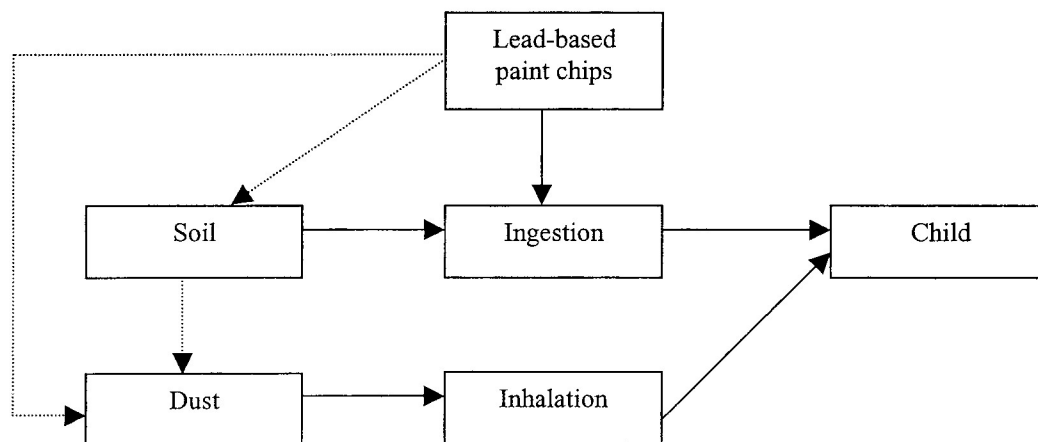


Figure 1. Lead-Based Paint as a Direct and Indirect Source of Lead Exposure in Children

Charney et al. (1980) concluded that in inner city children, lead-based paint, lead-contaminated soil, and interior dust were all significantly correlated with the ingestion of lead and the subsequent elevation in blood lead levels.

It is estimated that 12 million children are potentially exposed to harmful levels of lead found in paint, and approximately 5.9 to 11.7 million children are exposed to lead through contaminated dust and/or soil (Xintaras, 1992). Children under the age of six have an increased risk for lead poisoning. For this age group, the increased susceptibility to the effects of lead is a result of several factors including incomplete development of the blood-brain barrier, increased hand-to-mouth activity (resulting in the ingestion of paint chips, soil and dust), increased absorption of lead by the gastrointestinal tract, and nutritional deficiencies that may enhance lead absorption (Xintaras, 1992).

gastrointestinal tract, and nutritional deficiencies that may enhance lead absorption (Xintaras, 1992).

Housing age is a significant predictor of soil lead levels (EPA, 1996). Most of the lead-based paint in the United States was manufactured prior to 1950 (H.W. Mielke & Regan, 1998). Voluntary standards within industry during the 1950s worked to limit the content of lead in paint (Frankel, 1994); however, lead was not banned in paint until the late 1970s (Jacobs et al., 2002). Therefore, housing units built prior to 1950 have the greatest likelihood of having surfaces painted with lead-based paint, and houses built between 1950 and 1978 have a greater chance of having lead-based paint compared to newer homes (Kassa & Bisesi, 2000). Thus, children living in housing units built prior to 1950 have an increased risk for lead poisoning (Brown, Shenassa, & Tips, 2001). Moreover, higher levels of lead in soil and dust are found in housing units with deteriorating exterior paint (Jacobs et al., 2002).

By examining the soil lead levels in older homes, the relative risk to children living in these homes can be approximated. The purpose of this study, therefore, is to examine soil lead levels in older homes located in a nationally recognized historic district in a South Central city in Kentucky as the first step in examining the public health risk that may exist among children in this area. Like many other older neighborhoods across the United States, this district is currently experiencing gentrification. As younger families relocate to this district, the potential for lead poisoning in children increases as the number of children present increases. The gentrification is responsible for the extensive renovations ongoing in this district. Renovations such as paint stripping could potentially

increase the amount of lead present in the soil, and thus increase the exposure of lead to children in this area.

The extent to which the homeowners are aware of the existence of lead on their property or its harmful effects is not known. Similarly, preventative measures can be outlined to reduce exposure for adults and especially children. Because this neighborhood is currently undergoing renovations, educational efforts can also be targeted toward workers on these projects to increase awareness and further protect humans and the environment.

Research Questions

Because soil lead levels can be predictive of childhood blood lead levels and various factors contribute to the amount of lead in the soil, the following research questions have been posed: Is age of housing unit predictive of soil lead levels? Does the exterior composition of homes affect the amount of lead in the soil? Does paint loading affect soil lead levels?

Hypotheses

The relationship between housing age and soil lead levels will be examined by testing Hypothesis 1.

H_0 : There will be no correlation between housing age and soil lead levels.

It is predicted that housing age is a predictor of soil lead levels and thus a positive correlation will exist between the two.

The relationship between exterior and soil lead levels will be examined by testing Hypothesis 2.

H_0 : There will be no difference among soil lead levels by housing type (frame, brick and other).

It is predicted that frame housing units will have higher soil lead levels.

The relationship between paint loading and soil lead levels will be examined by testing Hypothesis 3.

H_0 : There will be no difference among soil lead levels by paint loading (fully painted vs. non-painted).

It is predicted that the greater the area of painted surfaces, the higher the lead levels will be, and thus housing units that are fully painted will have higher levels than those that are not.

CHAPTER 2

LITERATURE REVIEW

Definition of Lead Poisoning

Over the years, the Centers for Disease Control and Prevention (CDC) has revised its definition of the action level of lead—the level at which interventions and further monitoring must occur—in blood (Muir & Campbell, 1995). Prior to 1970, the action level set by the CDC was 60 $\mu\text{g}/\text{dl}$. In 1978, the level was lowered to 30 $\mu\text{g}/\text{dl}$, and then lowered again to 25 $\mu\text{g}/\text{dl}$ in 1985. Today, the action level for lead in blood is 10 $\mu\text{g}/\text{dl}$. However, studies show that adverse effects in children can occur at concentrations lower than the current action level (Muir & Campbell, 1995). Figure 2 shows the decline in actions levels set by the CDC from 1960 to the present.

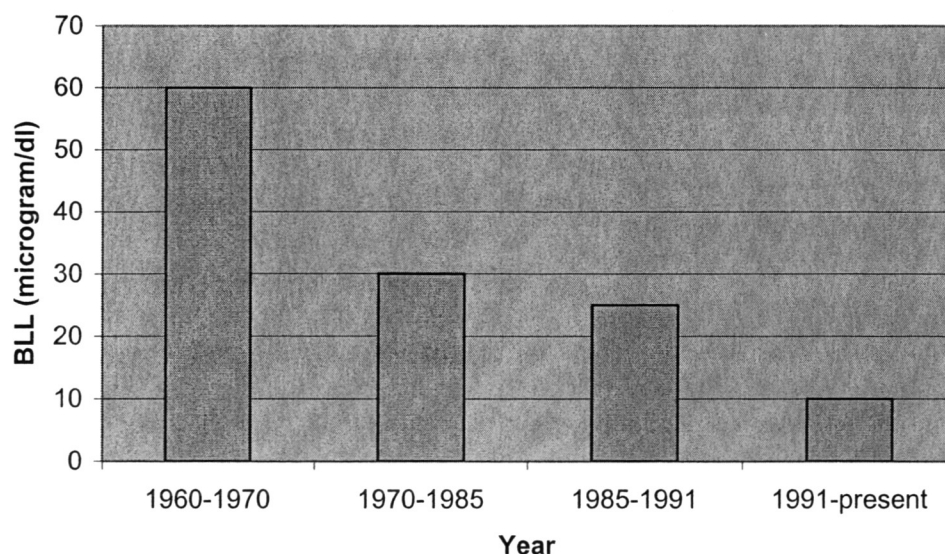


Figure 2. Decline in Blood Lead Action Levels

Incidence of Childhood Lead Poisoning

Despite earlier recognition in other countries, lead poisoning was not recognized as an issue plaguing public health in the United States until around 1917 (Elhelu & Caldwell, 1995). From 1978 to 1998, approximately 200 deaths in the United States were linked to lead poisoning (Kaufmann, Staes, & Matte, 2003). Childhood blood lead levels peaked during the 1970s. The Second National Health and Nutrition Examination Survey (NHANES II) conducted from 1976-1980 reported the mean blood lead levels in children ages one to five was 14.9 $\mu\text{g}/\text{dl}$ (“Children’s Blood Lead Levels,” 2003). The same study reported that approximately 88.2% of children in the United States ages one to five had lead levels that exceeded the action levels set by the CDC (“Children’s Blood Lead Levels,” 2003).

In 1978, the United States Environmental Protection Agency (EPA) reported that the number of children in the United States with elevated blood levels reached three to four million (EPA, 2002). During the 1990s, that number declined to approximately 890,000 and declined further to 434,000 between the years 1999 and 2000 largely in part to efforts by the EPA and CDC (EPA, 2002). Figure 3 depicts the decline in the number of children with blood lead levels $> 10 \mu\text{g}/\text{dl}$ from the years 1976 to 2000.

In 1988, only 8.9% of U.S. children had levels above the CDC standard. (EPA, 2001a). The geometric blood lead levels of children in the United States dropped from 2.7 $\mu\text{g}/\text{dl}$ during the years 1991-1994 to 2.2 $\mu\text{g}/\text{dl}$ in during 1999 and 2000 (EPA, 2001a). Figure 4 illustrates the decline in the geometric mean blood levels of children ages one to five as reported by the NHANES.

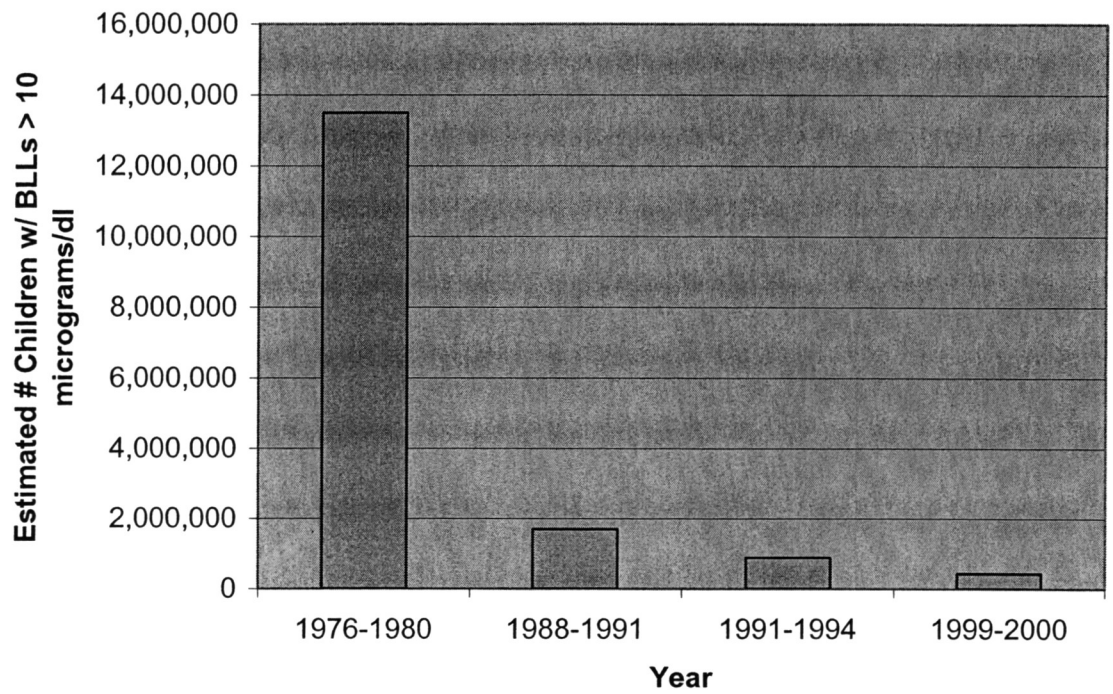


Figure 3. Estimated Number of Children with Blood Lead Levels > 10 µg/dl

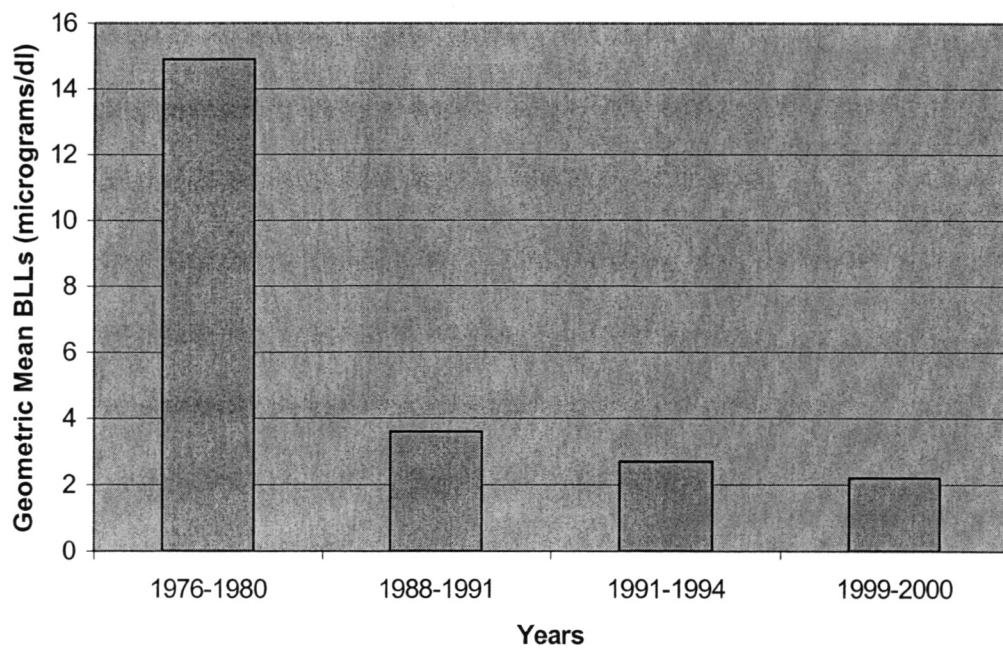


Figure 4. Geometric Mean Blood Lead Levels in Children Aged 1-5

Health Effects of Lead

Lead poisoning affects both children and adults. Lead exposure in adults is primarily occupational; however, childhood exposure to lead predominantly occurs from through environmental contact and remains a leading environmental problem affecting children today (“Health Effects of Lead in Children and Adults,” 1999).

Lead affects a number of organ systems in the body including the liver, kidneys, blood, and nervous system. The effects of lead are primarily chronic; however, acute lead poisoning does occur (World Bank Group, 1999). At levels of 80 $\mu\text{g}/\text{dl}$ in children and 100 $\mu\text{g}/\text{dl}$ in adults, lead encephalopathy may occur. At levels ≥ 70 $\mu\text{g}/\text{dl}$, seizures, coma, and even death may occur. One acute effect, lead colic, which includes damage to the gastrointestinal tract, may occur at levels as low as 50 $\mu\text{g}/\text{dl}$ (World Bank Group, 1999). Lead levels between 10 $\mu\text{g}/\text{dl}$ and 30 $\mu\text{g}/\text{dl}$ do not usually produce obvious symptoms, making diagnosing lead poisoning difficult for physicians (Muir & Campbell, 1995). Identifiable symptoms usually occur between 35 and 50 $\mu\text{g}/\text{dl}$ in children and 40 and 60 $\mu\text{g}/\text{dl}$ for adults. The chronic effects of lead poisoning are initially hard to diagnose because the symptoms, including headache, malaise, and abdominal pain, are common to other illness (Muir & Campbell, 1995).

Neurological Effects

Lead affects the central and peripheral nervous systems in both children and adults. Children younger than six years, however, are especially vulnerable to the neurological effects of lead because of the incomplete development of the neurological system (EPA, 2001). Studies have shown that blood lead levels and cognitive development are inversely related (Bellinger, Leviton, Waternaux, Needleman & Rabinowitz, 1991;

Fulton et al., 1987; Dietrich, Kraft, & Bornschein, 1987; McMichael et al., 1988), and that even low levels of lead--once thought to be non-problematic--can produce effects such as decreased intelligence and attention span, learning disabilities, as well as behavioral problems (Lead Based Paint Hazard Reduction and Financing Task Force, 1995). These cognitive effects tend to persist: children with high blood lead levels at 24 months scored lower on the McCarthy Scales of Children's Abilities at 57 months compared to children with normal blood lead levels (Elhelu & Caldwell, 1995).

Other Effects

In addition to neurological effects, lead has negative effects on blood formation. Lead slows the maturation of red blood cells and inhibits the formation of hemoglobin, which may result in anemia (Muir & Campbell, 1995). Lead also affects the filtering capabilities of the kidney ("Health Effects of Lead in Children and Adults," 1999). As the kidney is damaged, the filtering efficiency is lost which can result in hypertension. Other effects of lead include spontaneous abortions and stillbirths as well as decreased sperm counts (Moore, 2002). Additionally, the International Agency for Cancer Research has labeled lead as a possible human carcinogen based on results from animal studies (CDC, 2003).

Predictors of Soil Lead Contamination

Housing age, condition of the exterior painted surface, and area patterns of lead contamination have been observed to have a relationship with soil lead concentrations (United States Department of Housing and Urban Development [HUD], 2001).

According to the 1988 Lead-Based Paint Hazard Reduction Act (commonly called Title

X), a lead-based paint hazards is “any condition that causes exposure to lead from lead-contaminated dust, bare, lead contaminated soil; lead-based paint that is deteriorated; or lead-based paint on accessible surfaces, friction surfaces, or impact surfaces” (HUD, 2001 p. 3-1). Of the 26 million houses with lead-based paint hazards, six million had soil lead hazards (HUD, 2001).

Housing Age

Lead-based paint hazards and increased soil lead levels are consistently higher among older homes (HUD, 2001). In 2001, approximately 26 million homes in the United States had significant hazards resulting from lead-based paint (HUD, 2001). Housing units built prior to 1940 show the greatest concentrations of lead in the soil (HUD, 2001; Jacobs et al., 2002). Findings from a 2001 National Survey of Lead and Allergens in Housing show that 67% of housing units built before 1940 had soil lead levels ≥ 400 parts per million (ppm) while only 31% of housing units built between 1940 and 1959 had similar levels (HUD, 2001). As shown in Table 1, 31% of housing units constructed prior to 1940 had levels $\geq 1,200$ ppm, and 19% of housing units built between 1940 and 1959 had similar soil concentrations (HUD, 2001). In the same study, soil lead levels greater than or equal to 5,000 ppm were found in 11% of houses built before 1940 and in 4% of houses built between 1940 and 1959 (HUD, 2001).

Table 1: Percentage of Housing Units with Higher Soil Lead Levels by Age of Construction.

Age of Construction	Percentage of units with soil lead levels	
	<u>≥ 400 ppm</u>	<u>$\geq 1,200$ ppm</u>
Prior to 1940	67%	37%
1940-1959	31%	19%
1960-1977	9%	3%
1978-1998	0%	0%

Using a smaller study population and the same premise, Jacobs et al. (2002) reported similar results. Because the study population was smaller than that of the National Survey of Lead and Allergens in Housing (2001), the disparity between construction years and soil lead levels was less. The percentage of houses with soil lead levels ≥ 400 ppm but built during different time periods were similar (19% built before 1940 and 14% built between 1940 and 1959) (HUD, 2001). Thus, as housing age increases, soil lead levels increase as well. In support, Francek (1992) found that homes in Mt. Pleasant, Michigan, less than 20 years old had a median soil lead concentration of 200 ppm; units 20-100 years old, 960 ppm, and units greater than 100 years old had a median soil concentration of 1,040 ppm.

The decrease in soil lead levels in newer homes can be attributed in part to action taken against lead as well as federal legislation. In 1978, the Consumer Product Safety Commission removed lead from household paints. Amendments to the 1978 Lead-Based Poisoning Prevention Action called upon the Secretary of Housing and Urban Development to provide an estimate of the number of housing units in the United States with lead hazards (EPA, 1996), and provisions of Title X required the federal government

to identify and control lead hazards present in federally owned and assisted housing (EPA, 1998a).

In 1996, the United States EPA attempted to compare soil lead levels in publicly and privately-owned housing units respective of year of construction (EPA, 1996).

Approximately 23% of privately-owned units built prior to 1980 had soil levels ≥ 400 ppm; 8% had levels $\geq 1,200$ ppm, and 3% had levels of or exceeding 5,000 ppm (EPA, 1996). Percentage of housing units was not disaggregated further based on year of construction. Caution should be exercised when comparing this study with other studies similar in nature (e.g., Jacobs et al., 2002 and HUD, 2001). First, in the EPA study, data concerning publicly owned housing was not included because the sample of publicly owned units was not deemed representative of publicly owned housing units in the United States. In other studies, there is no mention of a distinction between publicly and privately owned housing units. Secondly, it may not be wise to compare the results of the EPA study with those previously mentioned because of the disparity in disaggregating the time frame in which the housing units were constructed. The majority of research uses a construction year classification scheme similar to those used by Jacobs et al. (2002) and HUD (2001). Here, the EPA combined all housing units built prior to 1980 into one category. The rationale for doing so is that paint containing lead was banned in 1978; therefore, housing units built before 1980 have a greater chance of containing lead and having higher soil lead concentrations compared to those houses built after 1980. The classification scheme of Jacobs et al. (2002) and HUD (2001) allows for a more in depth examination of the trends in soil lead concentrations. These trends parallel legislation and federal action aimed at reducing the amount of lead in paint.

Condition of Exterior Surface

Exterior painted surfaces and the condition of these surfaces is also associated with soil lead levels. Through the process of weathering, paint flakes or chips may fall onto the soil surface. The 1989-1990 National Lead Survey concluded that the probability of finding higher amounts of lead on a property is four to five times higher with the presence of exterior lead-based paint (Rogers, Clickner, Vendetti, & Rinehart, 1993). In particular, deteriorating lead-based paint is a strong statistical predictor of lead in the soil (Rogers et al., 1993) and is more likely to be found in older homes (Jacobs et al., 2002). Approximately 17 million housing units in the United States have some form of deteriorating lead-based paint (HUD, 2001). During the National Survey of Lead and Allergens in Housing, HUD (2001) found that 56% of houses built prior to 1940 have deteriorating lead-based paint compared to 32% built between 1940 and 1959 as shown in Table 2.

Table 2: Percentage of Housing Units with Deteriorating Paint by Age of Construction.

Age of Construction	Percent housing units with deteriorating paint
Prior to 1940	44%
1940-1959	25%
1960-1977	2%
1978-1998	0%

Bare soil lead levels are highest in housing units with deteriorating lead-based paint (HUD, 2001). The percentage of houses with deteriorating lead-based paint that have soil lead levels $\geq 1,200$ ppm is considerably higher than those without deteriorating lead-based paint (24% vs. 4%, respectively) (HUD, 2001; Jacobs et al., 2002). Borschein (1986) found that homes built during the 19th century and having deteriorating lead-based

paint have a high geometric mean concentration of lead in the soil. However, in a 1990 study in Mt. Pleasant, Michigan, although arithmetic mean soil lead levels were highest in housing classified as being in fair or poor condition, the author concluded that when comparing soil lead levels near houses in good or excellent with those in poor or fair condition, there is no significant difference (Francek, 1992).

Patterns of Soil Lead Distribution

As paint chips fall off of the exterior wall, they are deposited into the soil. Because lead in soil has a half-life of 1,000 years, the paint chips, for the most part, remain intact and close to the initial deposition site (Krueger, 1989). Thus, concentrations are highest in these areas. As the distance from the foundation increases, soil lead levels decrease (Rogers, et al., 1993; Schmitt, Trippler, Walcher, & Lund, 1988). In a study of five Minnesota cities, Schmitt et al. (1988) collected samples near the house foundation and in the backyard (away from the foundation). In every city, the geometric mean soil lead concentrations were considerably higher nearest the housing unit, and almost all of the soil lead concentrations greater than 1,000 and 2,000 ppm were found in soils collected near the foundations of the housing units. A similar study conducted in New Haven, Connecticut examined housing age and soil concentrations near to and far away from the housing units. For homes built prior to 1940, soil concentrations were highest near the housing unit (Stark, Quah, Meigs, & DeLouise, 1982). However, as housing age became newer, a trend developed in which soil concentrations became lower near the housing unit and increased with increasing distance from the unit. One explanation for the decrease in soil lead concentrations near housing units could be the voluntary reduction

in lead content of paints beginning in the 1950s. However, this explanation does not explain the high levels that remained farther away from the housing unit. Studies have shown that lead levels increase near roadways due to automobile emissions (Elhelu & Caldwell, 1995; Franz & Hadley, 1981; H.W. Mielke, Dugas, & P.W. Mielke Jr., 1997; H.W. Mielke & Reagan, 1998).

Predictors of Childhood Blood Lead Levels

Housing age and the amount of lead in the soil have been shown to be significant predictors of blood lead levels in children. Housing age is a statistically strong predictor of lead-based paint hazards (HUD, 2001). The association between blood lead levels in children and housing age has been shown to be as strong as the association between age of housing and soil lead levels.

Phase 2 of NHANES III (1991-1994) showed that the geometric mean for children ages one to five living in housing units built prior to 1946 was 3.79 $\mu\text{g/dl}$ and 2.81 $\mu\text{g/dl}$ for those children living in units built between 1946 and 1976. The percentage of children with blood lead levels $\geq 10 \mu\text{g/dl}$ decreased with newer housing units (United States EPA, 1998b). Elevated blood lead levels were associated with older homes in Jefferson County, Kentucky. Approximately 28% of the study population living in older homes (coded as pre-1950) had elevated blood lead levels compared to only 9% living in newer homes (coded as post-1950) with similar blood levels. The geometric mean blood lead concentration was also higher for those children living in older homes (6.4 $\mu\text{g/dl}$) compared to children living in newer homes (4.3 $\mu\text{g/dl}$) (Kim, Stanley, & Buchanon, 2002). However, in one study by H.W. Mielke, Adams, et al. (1989), the author notes

“[t]here is no discernible general pattern between the age of the dwelling within a community and the lead concentrations of either the soil or the blood of the childhood population” (p. 264).

Compared to housing age, soil lead concentration is a stronger predictor of childhood blood lead levels, and thus has been more widely studied. The association between soil lead level and blood lead levels was stronger--by 12 orders of magnitude--than that of housing age and blood lead levels (H.W. Mielke, Dugas, & P.W. Mielke Jr., 1997). Mielke & Reagan (1998) noted that blood lead levels in children varied in the same direction as levels of lead in the soil but not with housing age. Thus soil lead is a stronger predictor of blood lead levels in children than housing age (H.W. Mielke, Dugas, & P.W. Mielke Jr., 1997). In one study, only a weak correlation was found between soil lead levels and soil lead levels (Bates et al., 1995); however, Charney et al. (1980) noted that children with high levels of lead in their blood also had a higher mean and median concentration of soil around than homes compared to children with lower blood lead levels. The presence of lead-based paint on the exterior of the housing unit may be used as a predictor of soil lead concentration and subsequently childhood blood lead levels. However, some children have elevated blood lead levels despite living in brick homes with no exterior paint. These elevated blood lead levels have been attributed to children playing in areas such as their backyards and playgrounds where contaminated soil could be present (Mason, 2002).

Soil lead concentrations have shown to vary according to the composition of the exterior surface. Schmitt et al. (1988) sampled soil from 213 units with wood exteriors

and 88 with brick. The geometric mean of the houses with wood exteriors was 522 ppm and 158 ppm for units with brick exteriors.

In a study in New Haven, Connecticut, the presence of soil lead near the home was one of the most important predictors of blood lead levels of children in the study population (Stark et al., 1982). Based on a study in Minnesota, the conclusion was made that the concentration of lead in the soil located in cities and the concentration of lead in the blood of children located in these cities vary in a “lock-step manner” with one another (Schmitt et al., 1982).

Additional support is provided through the seasonal influences that accompany childhood lead exposure. The amount of lead on the hands of children increases after playing outdoors, and the greater amount of lead in the soil, the more that appears on children’s hands (Yiin, Rhoads, & Lioy, 2000; H.W. Mielke, Dugas, & P.W. Mielke Jr., 1997). Charney et al. (1980) noted that higher levels of lead on the hands of children were associated with higher blood lead levels in these children. Because children are outdoors more during the summer months, their exposure to lead increases and the highest blood lead levels in children are observed during the summer (Yiin et al., 2000)

Researchers disagree on what extent lead-contaminated soil has on blood lead levels in children. The quantitative relationship is often described as a dose-response relationship where a change in the concentration of lead in the soil is accompanied by a subsequent change in blood lead levels (Xintaras, 1992). It is agreed upon that an increase in soil lead causes an increase in blood lead levels. The assumption is made that the relationship between soil lead concentrations and blood lead levels is a linear relationship; however, studies have shown that the relationship is not linear (Xintaras,

1992). In some studies, at high lead concentrations in the soil, the rate at which blood lead levels increase begins to fall off (Xintaras, 1992). Using data from studies conducted in Montana and Idaho, Schilling and Bain (1988) derived a model for the correlation that exists between blood lead levels and levels of lead in the soil:

$$\ln(\text{blood lead level}) = 0.879 + 0.241 \ln(\text{soil lead level}).$$

Using this model, an approximate increase of 1,000 ppm of lead in the soil would correspond to an approximate 6.0 $\mu\text{g/dl}$ increase in the level of lead in the blood (Xintaras, 1992). However, using a non-threshold, multiple linear regression model, Schilling and Bain (1988) estimated that there was an increase of 0.231 $\mu\text{g/dl}$ for the blood lead level (mean \ln) with every incremental unit increase in the soil lead level (mean \ln). H.W. Mielke, Anderson, et al. (1983) concluded that a soil lead concentration of 100 ppm may contribute to greater than 100% of the daily intake of lead per gram of soil that is permissible for infants.

CHAPTER 3

METHODS

Study Area

A nationally recognized historic district in the selected South Central Kentucky city was chosen as the study area. This district is currently undergoing gentrification and renovations. All housing units in the study area were built prior to 1950.

Before collecting soil samples, residents were asked for permission to include their houses in the study. Residents were contacted via door-to-door solicitations ($\underline{n} = 20$) and through mass recruitment at a picnic sponsored by the neighborhood association ($\underline{n} = 10$). Residents were briefed on the purpose of the study and the possible implications. Those choosing to participate were then asked to sign an informed consent (Appendix A).

Procedures

Surface and subsurface (1/2 to 1 inch deep) soil samples were collected using a stainless steel trowel. Soil samples were prepared according to EPA Method 6200 (Appendix B). Samples were collected approximately two feet from the foundation of the housing unit. When it was not possible to collect samples from this distance (due to mulching, concrete, etc.), samples were collected as close to the unit as possible ($\underline{n} = 4$). The samples were bagged and taken to the lab for preparation and analysis.

Ambient conditions are required for on-site testing. Results are less accurate when readings are taken from frozen ground or when air temperature is less than 40°F (EPA, 2001b). Soil moisture may also cause inaccurate readings as well as damage the

instrument. To control for these factors, samples were collected on dry days and the samples were dried and sieved according to protocol.

Measures

Measures for this project include three demographic items and the analytical measure of the soil. The following represent the measures used for this project.

Age of Housing Unit

Housing age was measured as a continuous variable. As part of the informed consent, residents were asked to provide information regarding the year of construction of their housing unit. Most homeowners were able to approximate the year of construction ($n = 25$). For those units where the residents did not provide a year of construction, this data was obtained from a brochure published by the historic district ($n = 3$). Year of construction was unavailable for two housing units. Housing age was calculated by subtracting the year of construction from the current year (2003). Housing age was categorized according to the following: 1) < 80 years old, 2) 80-99 years old, 3) 100-119 years old, 4) 120-139 years old, and 5) ≥ 140 years old.

Soil Lead Levels

Soil lead levels were measured as a continuous variable. Levels were measured using a NITON X-ray Fluorescence Spectrum Analyzer (XRF), which contains a Cadmium-109 source suitable for measuring lead (Sackett & Martin, 1988), following EPA Method 6200 (Appendix B). The XRF measured each soil sample for 120 nominal seconds (machine seconds). Soil lead levels were categorized according to categories set by the

EMPACT Lead Safe Yard Program in accordance with Toxic Substance Control Act (TSCA) Section 403. These categories are 1) Very High (> 5000 ppm), 2) High (2000-5000 ppm), 3) Moderately High (400-2000 ppm), and 4) Low or Urban Background (< 400 ppm) (EPA, 2001a; EPA, 2001b). Three of the soil samples were below the detection limits of XRF machine. The XRF reported these readings as < 41.0, < 44.0, and < 45.0 ppm. Since the true levels of lead are not known for these three samples, the values of 41.0, 44.0, and 45.0 ppm were used, respectively.

Exterior Surface

As soil samples were collected, the exterior surface composition of each housing unit was noted. Exterior surfaces were coded as follows: 1) frame, 2) brick, and 3) other.

- 1) Frame Housing Units. Frame houses included all those units with complete wood exteriors.
- 2) Brick Housing Units. Units coded as brick included all units with fully brick exteriors. Included in this category were brick homes that were fully painted and those non-painted. One house included in this category was a combination of brick and stone.
- 3) Other Housing Units. The remainder of the housing units was coded as other. Characteristics of housing units in this category included ones with aluminum/vinyl siding, rock, and houses that were a combination of compositions (e.g., wood and brick).

Paint Loading

During collection of soil samples, documentation was made regarding the extent of painted surfaces on the housing units. All of the housing units had some form of baseline painted surface. For purposes of this study two categories of paint loading were derived:

1) fully painted and 2) non-painted.

1) Fully Painted. Fully painted housing units were those housing units that had fully painted exteriors. Included in this category were both frame and brick houses that were fully painted.

2) Non-Painted. Those housing units that did not have fully painted exterior surfaces but had another form of baseline paint only were included in this category. This baseline paint included painted trim, columns, porches, etc. Included in this category were brick housing units not fully painted but with some exterior painted surfaces. Also included in this category were two housing units with wood and brick exteriors. While the brick portion of these housing units was not painted, the frame portion was.

Data Analysis

Descriptive Statistics

Frequency distributions and measures of central tendency were computed for categorical and continuous variables, respectively. To better describe the distribution of the soil lead levels, geometric means were calculated for the soil lead levels. All data was entered into SPSS. For inferential statistics, an alpha (α) of 0.1 was used.

Inferential Statistics

Inferential statistics were performed to test hypotheses. To test Hypothesis 1, which states that no correlation exists between housing age and soil lead levels, a Pearson's Correlation was computed for age of housing and soil lead levels. To test Hypothesis 2 (no difference in soil lead levels exists among frame, brick, and other housing units), an Analysis of Variance (ANOVA) was computed for soil lead levels and exterior category. To test Hypothesis 3, which states there is no difference between soil lead levels of fully painted and non-painted housing units, a t -test was computed for soil lead levels and paint loading. While the geometric mean was used to describe the distribution of the soil lead levels, arithmetic means were used when performing inferential statistics.

CHAPTER 4

RESULTS

Descriptive Statistics

Characteristics

Data regarding year of construction was available for 28 of the 30 housing units (93%). As shown in Table 3, the majority of the housing units were between 100 and 119 years old (43.0%, $n = 12$). Approximately 43.3% ($n = 13$) of the sample population had a brick exterior, and 53.3% ($n = 16$) were non-painted. As regards soil lead levels, most of the samples had low levels (39.7%, $n = 12$) while 23.1% ($n = 7$) had very high levels (see Appendix C for complete list of housing unit composition, year of construction and soil lead levels).

As shown in Table 4, the geometric mean (GM) for all housing units was 835.3 ($SD = 6.134$). Frame housing units had the highest geometric mean soil lead levels ($GM = 2702.8$, $SD = 6.094$), and houses that were fully painted had higher geometric mean soil lead levels ($GM = 1514.6$, $SD = 8.010$) compared to non-painted housing units. Figures 5 and 6 represent geometric mean soil lead levels by exterior composition and paint loading, respectively. Also, housing units that were between 120 and 139 years old had the highest geometric mean soil lead levels ($GM = 1824.9$, $SD = 5.087$) while houses less than 80 years old had the lowest levels ($GM = 327.9$, $SD = 1.467$). Figure 7 depicts the geometric mean soil lead levels by housing age.

Table 3

Characteristics of Sample

Characteristics	<u>n</u>	<u>%</u>
Age of Housing Units		
< 80 years old	2	7.2
80-99 years old	8	28.6
100-119 years old	12	43.0
120-139 years old	4	14.4
> 140 years old	2	7.2
Mean Age 108 years old		
<u>SD</u> = 19.661		
Exterior		
Frame	8	26.7
Brick	13	43.3
Other	9	30.0
Soil Lead Levels		
Low (< 400 ppm)	12	39.7
Moderately High (400-2000 ppm)	8	26.5
High (2000-5000 ppm)	3	9.9
Very High (> 5000 ppm)	7	23.1
Paint Loading		
Fully Painted	14	46.7
Non-Painted	16	53.3

Table 4

Geometric Mean Soil Lead Levels

Variable	<u>GM</u>	<u>(SD)</u>	<u>Range</u>
All Housing Units	835.3	6.134	41-27,000
Exterior			
Frame	2702.8	6.094	114-27,000
Brick	654.6	6.509	41-11,700
Other	418.3	3.812	45-6140
Paint Loading			
Fully Painted	1514.6	8.010	41-27,000
Non-Painted	506.4	4.29	45-9310
Age			
< 80 years old	327.9	1.467	250-430
80-99 years old	375.1	2.928	91.6-1280
100-119 years old	1247.9	10.475	44-27,000
120-139 years old	1824.9	5.087	299-11,700
> 140 years old	390.7	1.093	367-416

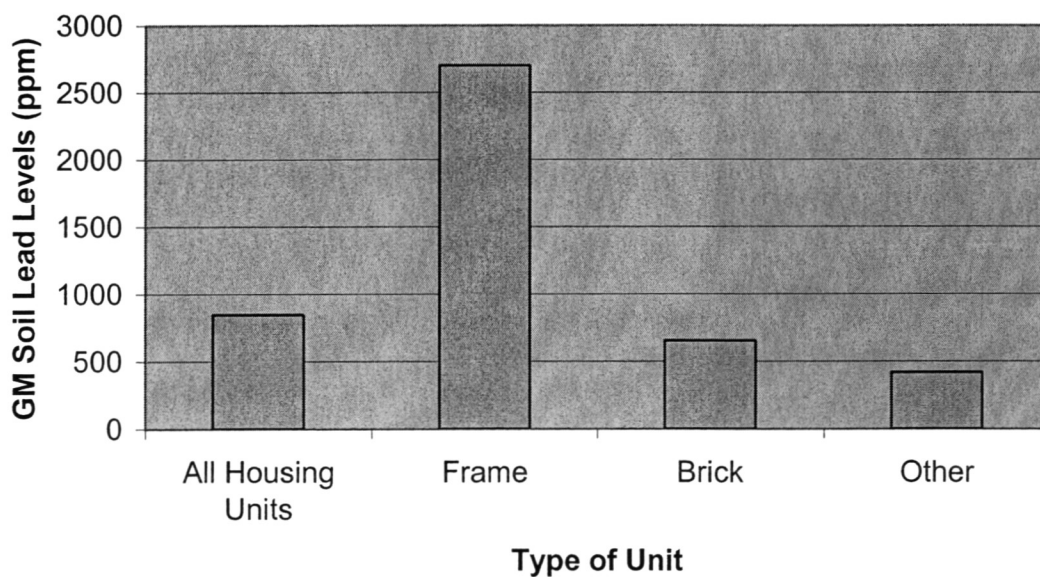


Figure 5. Geometric Mean Soil Lead Levels by Exterior

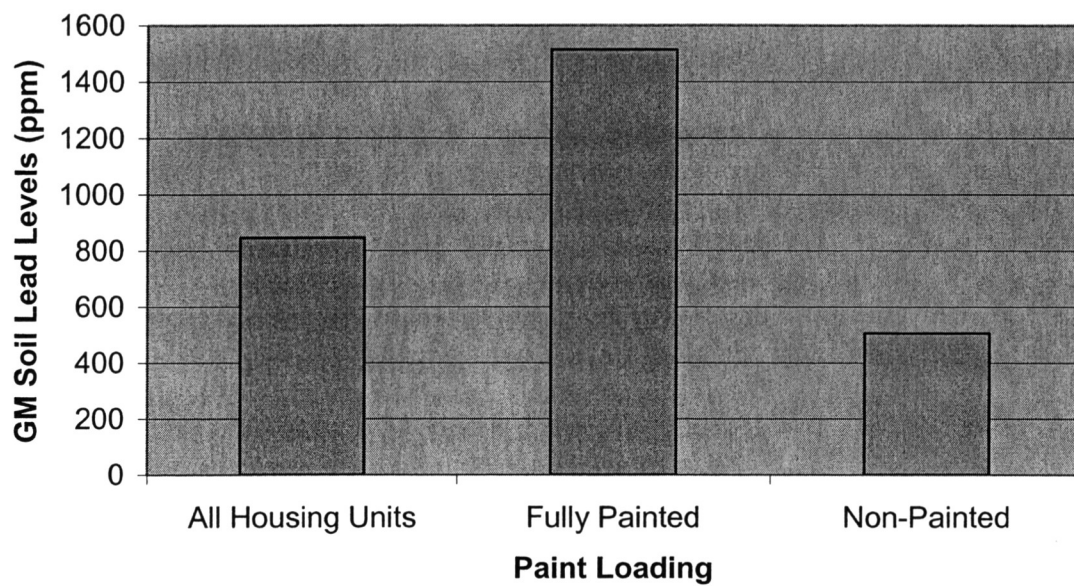


Figure 6. Geometric Mean Soil Lead Levels by Paint Loading

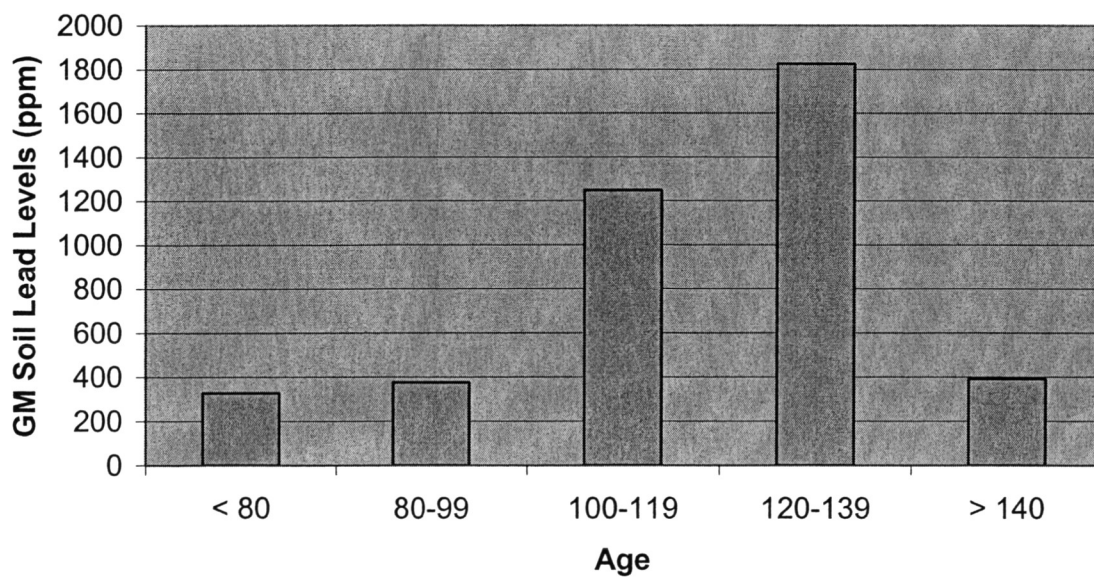


Figure 7. Geometric Mean Soil Lead Levels by Age.

Inferential Statistics

In this study inferential statistics were used to explore relationships between soil lead levels and 1) age, 2) exterior composition, and 3) paint loading. For purposes of this study, a 90% level of confidence was established because of the exploratory nature of this study and small sample size. To test Hypothesis 1 (no correlation exists between housing age and soil lead levels), a Pearson's Correlation was computed. There was no correlation detected ($r = 0.06$, $p = 0.763$). Therefore, Hypothesis 1 fails to be rejected: within this study there was no correlation between age of housing unit and soil lead levels.

To test Hypothesis 2, which stated that no difference in soil lead levels exists among frame, brick, and other housing units, an ANOVA was computed using soil lead levels as the dependent variable and the three exterior categories 1) frame, 2) brick, and 3) other as the independent variable. The overall model revealed a significant difference ($f = 3.293$, $df = 2,27$, $p = 0.053$) between the two variables. Therefore, Hypothesis 2 is rejected. As shown in Table 5, frame houses had the highest mean soil lead level ($\bar{x} = 7400.9$, $SD = 9357.7$). Soil lead levels were significantly higher ($p = 0.080$) among frame houses than brick houses ($\bar{x} = 2776.8$, $SD = 4053.4$). Soil lead levels were also significantly higher ($p = 0.018$) among frame houses than houses categorized as other ($\bar{x} = 941.2$, $SD = 1759.2$). However, there was no significant difference in soil lead levels among brick houses than houses classified as other.

To test Hypothesis 3, which stated there will be no difference in soil lead levels between fully painted and non-painted housing units, a t -test was performed. The results

were significant ($t = 16.551$, $df = 29$, $p = 0.000$). Therefore, Hypothesis 3 is also rejected. The results are presented in Table 6.

Table 5

One-Way ANOVAs for Soil Lead Levels by Exterior Composition

	Frame (F) <u>M</u>	Brick (B) <u>M</u>	Other (O) <u>M</u>	<u>p</u>	<u>LSD</u>
Soil Lead Levels	7400.9	2776.8	971.2	0.053	F > B, O

Table 6

t-Test Analysis of Soil Lead Levels by Fully Painted and Non-Painted Housing Units

Variable	Fully Painted <u>M</u>	Non-Painted <u>M</u>	<u>t</u>
Soil Lead Levels	5519.4	1447.7	16.551*

* $p < 0.1$

CHAPTER 5

DISCUSSION

The purpose of this study was to explore the relationship between lead levels of older homes and three variables: age of housing unit, exterior composition, and paint loading. There was no relationship between housing age and soil lead levels, therefore Hypothesis 1 failed to be rejected. There was a significant difference in the lead levels in the soils of frame and brick housing units as well as frame and other units. There was also a significant difference between the soil lead levels in units that were fully painted compared to units with only baseline paint. Hypotheses 2 and 3 were rejected.

Age of Housing Unit

All of the housing units in the sample were constructed prior to 1950. Most homes were between 100 and 119 years old. While studies have shown a correlation between housing age and soil lead levels (EPA, 1996; Jacobs et al., 2002; HUD, 2001) and commented on housing age as a predictor of soil lead levels, the results of this study showed no correlation between housing age and soil lead levels. One plausible explanation for the lack in correlation is that all of the housing units were built prior to 1950 when actions against lead-based paint began. No housing units built after this date were included in this study. Had newer housing units been included, a more thorough comparison of soil lead levels and housing age could have been made.

Exterior Surfaces

Much of the research on soil lead levels has focused on age of housing and the presence of exterior paint as predictors of lead in soil. Within this study, a significant difference did exist between frame and brick houses and frame and other. These findings support data collected by Schmitt et al. (1988). Not surprising, the highest soil lead level measured (27,000 ppm) was near a frame house. Soil lead levels were consistently higher among frame houses as compared to brick and other housing units. The higher levels could be due to the fact that frame houses have a greater painted surface area as compared to houses in the other categories. It is also worth noting that the soil from two of the frame houses had paint chips present in the sample. The levels of lead in the soil were 27,000 ppm and 5,610 ppm, respectively. Paint chips were also visible in the soil from one brick housing unit. The level of lead from this property was 9310 ppm. Another explanation why frame houses had higher geometric mean soil lead levels as compared to brick and other housing units is that the paint may adhere better to the brick and other surfaces as opposed to the wood frame.

Paint Loading

Research has shown that the presence of lead-based paint on the exterior surface of a housing unit is a contributor to lead in the soil and can be used as a predictor of blood lead levels in children. All of the housing units in the sample had some exterior painted surface. Grouping the housing units according to extent of paint loading (i.e., fully painted vs. non-painted) provided the opportunity to examine the extent to which paint loading affected soil lead levels. As expected, housing units with more paint had higher

loading affected soil lead levels. As expected, housing units with more paint had higher levels of lead than did those with less exterior paint. As more surface area is painted, the chances that paint chips will flake and contaminate the soil increases.

Limitations

Several limitations exist in this exploratory study. The sample size in this study was limited by the inability to contact several residents. The small sample size resulted in small cell sizes and prevented certain analyses from being performed. Future studies should include more participants. Because only housing units built prior to 1950 were used in this study, the full extent that age of housing unit had on soil lead levels was not examined. To examine this age factor, housing units built after 1950 would need to be included in the study. The convenience sample collected was also a limitation in this research. There is no assurance that this sample is representative of the entire housing population in the district.

The detection limit of the XRF is also a limitation in this study. For this study, the XRF detection limit was approximately 40 ppm. As discussed in the Methods section, three samples had levels below the detection limit. While the detection limitation is present in this study, the XRF was chosen for its advantages. Using the XRF is advantageous for on-site analysis. One advantage is that when treating contaminated soils, an XRF instrument can pinpoint locations of contamination, allowing those areas to be treated specifically rather than a whole yard or area. Another advantage is that using the XRF is cost-effective. XRF screenings do not involve sending a sample to a laboratory and the accompanying costs associated with doing so (e.g., lab fees and

shipping). A third advantage is the XRF is fast. Readings can be obtained in approximately two minutes compared to two weeks when samples are sent to a lab (Gray Environmental Inc.). Results have been shown to be comparable to those obtained in a laboratory (Clark, Menrath, Chen, Roda, & Succop, 1999; Reames & Lance, 2002). A last advantage is that XRF screenings can help guide investigations. Collecting data on-site with an XRF allows for the modification of plans in the field. Steps planned prior to the investigation can be omitted or altered if the XRF readings delegate doing so (Gray Environmental Inc.)

A final limitation involved the soil sampling frequency. One sample was collected from each housing unit. This sample was collected as close to the housing unit as possible and in bare soil whenever possible. The concentration of lead in that one sample may not be representative of the concentration in other locations on the property or for the property as a whole when considering other factors such as vegetation and the contribution of lead from other sources (e.g., automobile emissions). For future studies, several soil samples from various locations should be collected from the property and analyzed separately. The samples should then be combined to form a composite sample. This sample should be analyzed to represent soil lead concentrations for the entire property.

Future Studies

Future studies with the same premise as this study should explore whether similar concentrations of lead in soil exist in other historic districts or neighborhoods. While this researcher did not find a correlation between housing age and soil lead concentration,

future researchers may want to include newer housing units (constructed after 1950) to explore what effect, if any, age has on the amount of lead in the soil. This study did not find a significant difference in soil lead concentrations of some of the different exteriors (e.g., brick and other). Because few studies actually examine the relationship between exterior composition and soil lead levels, future studies should include more housing units of varying exteriors.

Finally, as regards soil lead levels as predictors of blood lead levels in children, future studies may include collecting blood samples from children living in residences where high levels of lead in soil may be expected or in older neighborhoods. These levels could be compared to soil lead levels and assess the relative impact soil lead has on childhood blood lead. If a childhood blood lead registry is available for a specific area, then only soil sampling would be necessary to compare the two variables.

Conclusions

In conclusion, this study sought to examine soil lead levels in older homes. Because soil lead can be used as a predictor of blood lead levels in children, conclusions can be made about the relative risk to children living in this district. The EPA defines lead as a hazard in soil if the concentration of lead is greater than 400 ppm in bare soils where children play or an average of 1,200 ppm for bare soils in the remaining areas of the property (EPA Issues New, More Stringent Hazards Defining Lead Hazards, 2001). Though the geometric mean soil lead level for all housing units was in the moderately high category, approximately ten housing units (33%) had soil lead levels that were high or very high. This result suggests that the risk for lead exposure in children is present in

this district. The overall higher levels in frame houses suggest that children living in these units are at the greatest risk. More conclusive research into children's blood lead levels in the district could assess the possible contribution of soil to these levels. As mentioned earlier, paint chips were present in three of the samples collected (two from frame houses and one from a brick house). Though these samples were thoroughly prepared before analysis, it is likely that the chips remained in the soil during analysis, thus causing higher soil lead readings. While the residents' perceived risk to lead exposure and the negative effects could not be ascertained in this study, the opportunity exists to increase public awareness about lead. Because the risk for lead exposure exists in this district, interventions should focus on educating residents about sources of lead exposure in the home environment, particularly the role soil can play in childhood lead exposure. In conjunction, interventions should also focus on practices, such as hand washing after playing outdoors, that could reduce exposure in children, as well as good practices regarding yard maintenance and renovations that would reduce the amount of lead present in the soil. Residents should also be aware that as more exterior surfaces are painted, the possibility of the soil being contaminated with lead increases.

Conclusions can also be drawn regarding the source of lead in the soil. Because the samples were collected near the housing unit, it is assumed that all other sources of lead (except for exterior paint) are negated.

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APPENDIX A

SOIL LEAD SAMPLING PERMISSION AGREEMENT

Soil Lead Sampling Permission Agreement

Your house and property have been selected to be included in a study entitled, "Analysis of Soil Lead Levels of Houses in Historic Districts of a South Central City." Your house was selected based on two criteria a) being built prior to 1950 and b) having an exterior painted surface. This study is being conducted as a Master's Thesis for Jason Cummins. This project will be done under the supervision of Dr. Rod Handy, a Western Kentucky University Professor. The study is designed to analyze the amount of lead in the soil. Lead has been shown to have negative effects for both adults and especially children. Lead in soil is an important pathway of childhood lead poisoning. Most of the lead in soil comes from the exterior of the house. With your permission, several soil samples (approximately ½ inch of the topsoil) will be collected and analyzed at a lab at Western Kentucky University. The only anticipated damage to occur to your property is the disturbance of the soil. Upon completing the study, you will be provided with a copy of the results of the lead analysis from your property, and any questions or concerns you have will be addressed at that time. During the course of the study if for any reason you decide not to participate, you may withdraw from the study. Thank you for your participation!

I _____ (printed name)
consent to the sampling of the soil on my property for lead. I assume responsibility for any minor damages that occur during the sampling activity. I understand that I may withdraw at any time during the study and that I will receive a copy of the results.

Signed _____ **Date** _____

Street Address _____

City, Zip Code _____

Telephone Number _____

Date of Construction _____

If at anytime you have any questions or concerns about this project, please contact Jason Cummins at 270-745-2015 (school) or 270-796-8840 (home). You may also contact Dr. Rod Handy at 270-745-6973.

APPENDIX B

EPA METHOD 6200: FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

Note: The following EPA Method 6200 was adapted from an original document found at <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6200.pdf> . The tables and figures from the original document were not included in this appendix.

METHOD 6200

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed in Table 1 for soil and sediment samples. Some common elements are not listed in Table 1 because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). They are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed in Table 1 are of environmental concern, while a few others have interference effects or change the elemental composition of the matrix, affecting quantitation of the analytes of interest. Generally elements of atomic number 16 or greater can be detected and quantitated by FPXRF.

1.2 Detection limits depend on several factors, the analyte of interest, the type of detector used, the type of excitation source, the strength of the excitation source, count times used to irradiate the sample, physical matrix effects, chemical matrix effects, and interelement spectral interferences. General instrument detection limits for analytes of interest in environmental applications are shown in Table 1. These detection limits apply to a clean matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (600-second) count times. These detection limits are given for guidance only and will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of field performance-based detection limits is presented in Section 13.4 of this method. The clean matrix and field performance-based detection limits should be used for general planning purposes, and a third detection limit discussed, based on the standard deviation around single measurements, should be used in assessing data quality. This detection limit is discussed in Sections 9.7 and 11.3.

1.3 Use of this method is restricted to personnel either trained and knowledgeable in the operation of an XRF instrument or under the supervision of a trained and knowledgeable individual. This method is a screening method to be used with confirmatory analysis using EPA-approved methods. This method's main strength is as a rapid field screening procedure. The method detection limits (MDL) of FPXRF are above the toxicity characteristic regulatory level for most RCRA analytes. If the precision, accuracy, and detection limits of FPXRF meet the data quality objectives (DQOs) of your project, then XRF is a fast, powerful, cost effective technology for site characterization.

2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use sealed radioisotope sources to irradiate samples with x-rays. X-ray tubes are used to irradiate samples in the laboratory and are beginning to be incorporated into field portable instruments. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This latter process is known as the photoelectric effect. When an atom absorbs the source x-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of x-rays characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

Three electron shells are generally involved in emission of x-rays during FPXRF analysis of environmental samples: the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given metal has multiple intensity peaks generated from the emission of K, L, or M shell electrons. The most commonly measured x-ray emissions are from the K and L shells; only metals with an atomic number greater than 57 have measurable M shell emissions.

Each characteristic x-ray line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α) or beta (β), which indicates the higher shell from which electrons fell to fill the vacancy and produce the x-ray. For example, a K_α line is produced by a vacancy in the K shell filled by an L shell electron, whereas a K_β line is produced by a vacancy in the K shell filled by an M shell electron. The K_α transition is on average 6 to 7 times more probable than the K_β transition; therefore, the K_α line is approximately 7 times more intense than the K_β line for a given element, making the K_α line the choice for quantitation purposes.

The K lines for a given element are the most energetic lines and are the preferred lines for analysis. For a given atom, the x-rays emitted from L transitions are always less energetic than those emitted from K transitions. Unlike the K lines, the main L emission lines (L_α and L_β) for an element are of nearly equal intensity. The choice of one or the other depends on what interfering element lines might be present. The L emission lines are useful for analyses involving elements of atomic number (Z) 58 (cerium) through 92 (uranium).

An x-ray source can excite characteristic x-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element, that is, the K absorption edge, L absorption edge, or M absorption edge energy. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K absorption edge energy is approximately the sum of the K, L, and M line energies of the particular element, and the L absorption edge energy is approximately the sum of the L and M line energies. FPXRF is more sensitive to an element with an absorption edge energy close to but less than the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.7 keV than to chromium, which has a K line energy of 5.41 keV.

2.2 Under this method, inorganic analytes of interest are identified and quantitated using a field portable energy-dispersive x-ray fluorescence spectrometer. Radiation from one or more radioisotope sources or an electrically excited x-ray tube is used to generate characteristic x-ray emissions from elements in a sample. Up to three sources may be used to irradiate a sample. Each source emits a specific set of primary x-rays that excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the source is selected according to its excitation efficiency for the element of interest.

For measurement, the sample is positioned in front of the probe window. This can be done in two manners using FPXRF instruments: in situ or intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. The sample cup is then placed on top of the window inside a protective cover for analysis.

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window

and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

The measurement time of each source is user-selectable. Shorter source measurement times (30 seconds) are generally used for initial screening and hot spot delineation, and longer measurement times (up to 300 seconds) are typically used to meet higher precision and accuracy requirements. FPXRF instruments can be calibrated using the following methods: internally using fundamental parameters determined by the manufacturer, empirically based on site-specific calibration standards (SSCS), or based on Compton peak ratios. The Compton peak is produced by backscattering of the source radiation. Some FPXRF instruments can be calibrated using multiple methods.

3.0 DEFINITIONS

3.1 FPXRF: Field portable x-ray fluorescence.

3.2 MCA: Multichannel analyzer for measuring pulse amplitude.

3.3 SSCS: Site specific calibration standard.

3.4 FP: Fundamental parameter.

3.5 ROI: Region of interest.

3.6 SRM: Standard reference material. A standard containing certified amounts of metals in soil or sediment.

3.7 eV: Electron Volt. A unit of energy equivalent to the amount of energy gained by an electron passing through a potential difference of one volt.

3.8 Refer to Chapter One and Chapter Three for additional definitions.

4.0 INTERFERENCES

4.1 The total method error for FPXRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in FPXRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are discussed below.

4.2 Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the FPXRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles

"settle" to the bottom of the sample cup, the analyte concentration measurement will be higher than if the fine particles are not mixed in well and stay on top of the coarser-grained particles in the sample cup. One way to reduce such error is to grind and sieve all soil samples to a uniform particle size thus reducing sample-to-sample particle size variability. Homogeneity is always a concern when dealing with soil samples. Every effort should be made to thoroughly mix and homogenize soil samples before analysis. Field studies have shown heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples.

4.3 Moisture content may affect the accuracy of analysis of soil and sediment sample analyses. When the moisture content is between 5 and 20 percent, the overall error from moisture may be minimal. However, moisture content may be a major source of error when analyzing samples of surface soil or sediment that are saturated with water. This error can be minimized by drying the samples in a convection or toaster oven. Microwave drying is not recommended because field studies have shown that microwave drying can increase variability between FPXRF data and confirmatory analysis and because metal fragments in the sample can cause arcing to occur in a microwave.

4.4 Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.

4.5 Chemical matrix effects result from differences in the concentrations of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as x-ray absorption and enhancement phenomena. Both effects are common in soils contaminated with heavy metals. As examples of absorption and enhancement effects; iron (Fe) tends to absorb copper (Cu) x-rays, reducing the intensity of the Cu measured by the detector, while chromium (Cr) will be enhanced at the expense of Fe because the absorption edge of Cr is slightly lower in energy than the fluorescent peak of iron. The effects can be corrected mathematically through the use of fundamental parameter (FP) coefficients. The effects also can be compensated for using SSCS, which contain all the elements present on site that can interfere with one another.

4.6 When present in a sample, certain x-ray lines from different elements can be very close in energy and, therefore, can cause interference by producing a severely overlapped spectrum. The degree to which a detector can resolve the two different peaks depends on the energy resolution of the detector. If the energy difference between the two peaks in electron volts is less than the resolution of the detector in electron volts, then the detector will not be able to fully resolve the peaks.

The most common spectrum overlaps involve the K_{β} line of element Z-1 with the K_{α} line of element Z. This is called the K_{α} / K_{β} interference. Because the K_{α} : K_{β} intensity ratio for a given element usually is about 7:1, the interfering element, Z-1, must be present at large concentrations to cause a problem. Two examples of this type of spectral interference involve the presence of large concentrations of vanadium (V) when attempting to measure Cr or the presence of large concentrations of Fe when attempting to measure cobalt (Co). The V K_{α} and K_{β} energies are 4.95 and 5.43 keV, respectively, and the Cr K_{α} energy is 5.41 keV. The Fe K_{α} and K_{β} energies are 6.40 and 7.06 keV, respectively, and the Co K_{β} energy is 6.92 keV. The difference between the V K_{β} and Cr K_{α} energies is 20 eV, and the difference between the Fe K_{β} and the Co K_{α} energies is 140 eV. The resolution of the highest-resolution detectors in FPXRF instruments is 170 eV. Therefore, large amounts of V and Fe will interfere with quantitation of Cr or Co, respectively.

The presence of Fe is a frequent problem because it is often found in soils at tens of thousands of parts per million (ppm).

4.7 Other interferences can arise from K/L, K/M, and L/M line overlaps, although these overlaps are less common. Examples of such overlap involve arsenic (As) K_{α} /lead (Pb) L_{α} and sulfur (S) K_{α} /Pb M_{α} . In the As/Pb case, Pb can be measured from the Pb L_{β} line, and As can be measured from either the As K_{α} or the As K_{β} line; in this way the interference can be corrected. If the As K_{β} line is used, sensitivity will be decreased by a factor of two to five times because it is a less intense line than the As K_{α} line. If the As K_{α} line is used in the presence of Pb, mathematical corrections within the instrument software can be used to subtract out the Pb interference. However, because of the limits of mathematical corrections, As concentrations cannot be efficiently calculated for samples with Pb:As ratios of 10:1 or more. This high ratio of Pb to As may result in no As being reported regardless of the actual concentration present.

No instrument can fully compensate for this interference. It is important for an operator to understand this limitation of FPXRF instruments and consult with the manufacturer of the FPXRF instrument to evaluate options to minimize this limitation. The operator's decision will be based on action levels for metals in soil established for the site, matrix effects, capabilities of the instrument, data quality objectives, and the ratio of lead to arsenic known to be present at the site. If a site is encountered that contains lead at concentrations greater than ten times the concentration of arsenic it is advisable that all critical soil samples be sent off site for confirmatory analysis by an EPA-approved method.

4.8 If SSCS are used to calibrate an FPXRF instrument, the samples collected must be representative of the site under investigation. Representative soil sampling ensures that a sample or group of samples accurately reflects the concentrations of the contaminants of concern at a given time and location. Analytical results for representative samples reflect variations in the presence and concentration ranges of contaminants throughout a site. Variables affecting sample representativeness include differences in soil type, contaminant concentration variability, sample collection and preparation variability, and analytical variability, all of which should be minimized as much as possible.

4.9 Soil physical and chemical effects may be corrected using SSCS that have been analyzed by inductively coupled plasma (ICP) or atomic absorption (AA) methods. However, a major source of error can be introduced if these samples are not representative of the site or if the analytical error is large. Another concern is the type of digestion procedure used to prepare the soil samples for the reference analysis. Analytical results for the confirmatory method will vary depending on whether a partial digestion procedure, such as SW-846 Method 3050, or a total digestion procedure, such as Method 3052 is used. It is known that depending on the nature of the soil or sediment, Method 3050 will achieve differing extraction efficiencies for different analytes of interest. The confirmatory method should meet the project data quality objectives. XRF measures the total concentration of an element; therefore, to achieve the greatest comparability of this method with the reference method (reduced bias), a total digestion procedure should be used for sample preparation. However, in the study used to generate the performance data for this method, the confirmatory method used was Method 3050, and the FPXRF data compared very well with regression correlation coefficients (r^2 often exceeding 0.95, except for barium and chromium. See Table 9 in Section 17.0). The critical factor is that the digestion procedure and analytical reference method used should meet the data quality objectives (DQOs) of the project and match the method used for confirmation analysis.

4.10 Ambient temperature changes can affect the gain of the amplifiers producing

instrument drift. Gain or drift is primarily a function of the electronics (amplifier or preamplifier) and not the detector as most instrument detectors are cooled to a constant temperature. Most FPXRF instruments have a built-in automatic gain control. If the automatic gain control is allowed to make periodic adjustments, the instrument will compensate for the influence of temperature changes on its energy scale. If the FPXRF instrument has an automatic gain control function, the operator will not have to adjust the instrument's gain unless an error message appears. If an error message appears, the operator should follow the manufacturer's procedures for troubleshooting the problem. Often, this involves performing a new energy calibration. The performance of an energy calibration check to assess drift is a quality control measure discussed in Section 9.2.

If the operator is instructed by the manufacturer to manually conduct a gain check because of increasing or decreasing ambient temperature, it is standard to perform a gain check after every 10 to 20 sample measurements or once an hour whichever is more frequent. It is also suggested that a gain check be performed if the temperature fluctuates more than 10 to 20 E F. The operator should follow the manufacturer's recommendations for gain check frequency.

5.0 SAFETY

5.1 Proper training for the safe operation of the instrument and radiation training should be completed by the analyst prior to analysis. Radiation safety for each specific instrument can be found in the operators manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. The analyst should be aware of the local state and national regulations that pertain to the use of radiation-producing equipment and radioactive materials with which compliance is required. Licenses for radioactive materials are of two types; (1) general license which is usually provided by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) specific license which is issued to named persons for the operation of radioactive instruments as required by local state agencies. There should be a person appointed within the organization that is solely responsible for properly instructing all personnel, maintaining inspection records, and monitoring x-ray equipment at regular intervals. A copy of the radioactive material licenses and leak tests should be present with the instrument at all times and available to local and national authorities upon request. X-ray tubes do not require radioactive material licenses or leak tests, but do require approvals and licenses which vary from state to state. In addition, fail-safe x-ray warning lights should be illuminated whenever an x-ray tube is energized. Provisions listed above concerning radiation safety regulations, shielding, training, and responsible personnel apply to x-ray tubes just as to radioactive sources. In addition, a log of the times and operating conditions should be kept whenever an x-ray tube is energized. Finally, an additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply. The danger of electric shock is as substantial as the danger from radiation but is often overlooked because of its familiarity.

5.2 Radiation monitoring equipment should be used with the handling of the instrument. The operator and the surrounding environment should be monitored continually for analyst exposure to radiation. Thermal luminescent detectors (TLD) in the form of badges and rings are used to monitor operator radiation exposure. The TLDs should be worn in the area of most frequent exposure. The maximum permissible whole-body dose from occupational exposure is Roentgen Equivalent Man (REM) per year. Possible exposure pathways for radiation to enter the body are ingestion, inhaling, and absorption. The best precaution to prevent radiation exposure is distance and shielding.

5.3 Refer to Chapter Three for guidance on some proper safety protocols.

6.0 EQUIPMENT AND SUPPLIES

6.1 FPXRF Spectrometer: An FPXRF spectrometer consists of four major components: (1) a source that provides x-rays; (2) a sample presentation device; (3) a detector that converts x-ray-generated photons emitted from the sample into measurable electronic signals; and (4) a data processing unit that contains an emission or fluorescence energy analyzer, such as an MCA, that processes the signals into an x-ray energy spectrum from which elemental concentrations in the sample may be calculated, and a data display and storage system. These components and additional, optional items, are discussed below.

6.1.1 Excitation Sources: Most FPXRF instruments use sealed radioisotope sources to produce x-rays in order to irradiate samples. The FPXRF instrument may contain between one and three radioisotope sources. Common radioisotope sources used for analysis for metals in soils are iron (Fe)-55, cadmium (Cd)-109, americium (Am)-241, and curium (Cm)-244. These sources may be contained in a probe along with a window and the detector; the probe is connected to a data reduction and handling system by means of a flexible cable. Alternatively, the sources, window, and detector may be included in the same unit as the data reduction and handling system.

The relative strength of the radioisotope sources is measured in units of millicuries (mCi). All other components of the FPXRF system being equal, the stronger the source, the greater the sensitivity and precision of a given instrument. Radioisotope sources undergo constant decay. In fact, it is this decay process that emits the primary x-rays used to excite samples for FPXRF analysis. The decay of radioisotopes is measured in "half-lives." The half-life of a radioisotope is defined as the length of time required to reduce the radioisotopes strength or activity by half. Developers of FPXRF technologies recommend source replacement at regular intervals based on the source's half-life. The characteristic x-rays emitted from each of the different sources have energies capable of exciting a certain range of analytes in a sample. Table 2 summarizes the characteristics of four common radioisotope sources.

X-ray tubes have higher radiation output, no intrinsic lifetime limit, produce constant output over their lifetime, and do not have the disposal problems of radioactive sources but are just now appearing in FPXRF instruments. An electrically-excited x-ray tube operates by bombarding an anode with electrons accelerated by a high voltage. The electrons gain an energy in electron volts equal to the accelerating voltage and can excite atomic transitions in the anode, which then produces characteristic x-rays. These characteristic x-rays are emitted through a window which contains the vacuum required for the electron acceleration. An important difference between x-ray tubes and radioactive sources is that the electrons which bombard the anode also produce a continuum of x-rays across a broad range of energies in addition to the characteristic x-rays. This continuum is weak compared to the characteristic x-rays but can provide substantial excitation since it covers a broad energy range. It has the undesired property of producing background in the spectrum near the analyte x-ray lines when it is scattered by the sample. For this reason a filter is often used between the x-ray tube and the sample to suppress the continuum radiation while passing the characteristic x-rays from the anode. This filter is sometimes incorporated into the window of the x-ray tube. The choice of accelerating voltage is governed by the anode material, since the electrons

must have sufficient energy to excite the anode, which requires a voltage greater than the absorption edge of the anode material. The anode is most efficiently excited by voltages 2 to 2.5 times the edge energy (most x-rays per unit power to the tube), although voltages as low as 1.5 times the absorption edge energy will work. The characteristic x-rays emitted by the anode are capable of exciting a range of elements in the sample just as with a radioactive source. Table 3 gives the recommended operating voltages and the sample elements excited for some common anodes.

6.1.2 Sample Presentation Device: FPXRF instruments can be operated in two modes: in situ and intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. For most FPXRF instruments operated in the intrusive mode, the probe is rotated so that the window faces upward. A protective sample cover is placed over the window, and the sample cup is placed on top of the window inside the protective sample cover for analysis.

6.1.3 Detectors: The detectors in the FPXRF instruments can be either solid-state detectors or gas-filled, proportional counter detectors. Common solid-state detectors include mercuric iodide (HgI₂), silicon pin diode and lithium-drifted silicon Si(Li). The HgI₂ detector is operated at a moderately subambient temperature controlled by a low power thermoelectric cooler. The silicon pin diode detector also is cooled via the thermoelectric Peltier effect. The Si(Li) detector must be cooled to at least -90 °C either with liquid nitrogen or by thermoelectric cooling via the Peltier effect. Instruments with a Si(Li) detector have an internal liquid nitrogen dewar with a capacity of 0.5 to 1.0 liter. Proportional counter detectors are rugged and lightweight, which are important features of a field portable detector. However, the resolution of a proportional counter detector is not as good as that of a solid-state detector. The energy resolution of a detector for characteristic x-rays is usually expressed in terms of full width at half-maximum (FWHM) height of the manganese K_α peak at 5.89 keV. The typical resolutions of the above mentioned detectors are as follows: HgI₂-270 eV; silicon pin diode-250 eV; Si(Li)-170 eV; and gas-filled, proportional counter-750 eV. During operation of a solid-state detector, an x-ray photon strikes a biased, solid-state crystal and loses energy in the crystal by producing electron-hole pairs. The electric charge produced is collected and provides a current pulse that is directly proportional to the energy of the x-ray photon absorbed by the crystal of the detector. A gas-filled, proportional counter detector is an ionization chamber filled with a mixture of noble and other gases. An x-ray photon entering the chamber ionizes the gas atoms. The electric charge produced is collected and provides an electric signal that is directly proportional to the energy of the x-ray photon absorbed by the gas in the detector.

6.1.4 Data Processing Units: The key component in the data processing unit of an FPXRF instrument is the MCA. The MCA receives pulses from the detector and sorts them by their amplitudes (energy level). The MCA counts pulses per second to determine the height of the peak in a spectrum, which is indicative of the target analyte's concentration. The spectrum of element peaks are built on the MCA. The MCAs in FPXRF instruments have from 256 to 2,048 channels. The concentrations of target analytes are usually shown in parts per million on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 100 to 500 sets of numerical analytical results. Most FPXRF instruments are menu-driven from software

built into the units or from PCs. Once the data-storage memory of an FPXRF unit is full, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery chargers.

6.3 Polyethylene sample cups: 31 millimeters (mm) to 40 mm in diameter with collar, or equivalent (appropriate for FPXRF instrument).

6.4 X-ray window film: Mylar TM , Kapton TM , Spectrolene TM , polypropylene, or equivalent; 2.5 to 6.0 micrometers (μm) thick.

6.5 Mortar and pestle: glass, agate, or aluminum oxide; for grinding soil and sediment samples.

6.6 Containers: glass or plastic to store samples.

6.7 Sieves: 60-mesh (0.25 mm), stainless-steel, Nylon, or equivalent for preparing soil and sediment samples.

6.8 Trowels: for smoothing soil surfaces and collecting soil samples.

6.9 Plastic bags: used for collection and homogenization of soil samples.

6.10 Drying oven: standard convection or toaster oven, for soil and sediment samples that require drying.

7.0 REAGENTS AND STANDARDS

7.1 Pure Element Standards: Each pure, single-element standard is intended to produce strong characteristic x-ray peaks of the element of interest only. Other elements present must not contribute to the fluorescence spectrum. A set of pure element standards for commonly sought analytes is supplied by the instrument manufacturer, if required for the instrument; not all instruments require the pure element standards. The standards are used to set the region of interest (ROI) for each element. They also can be used as energy calibration and resolution check samples.

7.2 Site-specific Calibration Standards: Instruments that employ fundamental parameters (FP) or similar mathematical models in minimizing matrix effects may not require SSCS. If the FP calibration model is to be optimized or if empirical calibration is necessary, then SSCSs must be collected, prepared, and analyzed.

7.2.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of ten samples spanning the concentration ranges of the analytes of interest and of the interfering elements must be obtained from the site. A sample size of 4 to 8 ounces is recommended, and standard glass sampling jars should be used.

7.2.2 Each sample should be oven-dried for 2 to 4 hours at a temperature of less than 150 E C. If mercury is to be analyzed, a separate sample portion must remain undried, as heating may volatilize the mercury. When the sample is dry, all large, organic debris and nonrepresentative material, such as twigs, leaves, roots, insects, asphalt, and

rock should be removed. The sample should be ground with a mortar and pestle and passed through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

7.2.3 The sample should be homogenized by using a riffle splitter or by placing 150 to 200 grams of the dried, sieved sample on a piece of kraft or butcher paper about 1.5 by 1.5 feet in size. Each corner of the paper should be lifted alternately, rolling the soil over on itself and toward the opposite corner. The soil should be rolled on itself 20 times. Approximately 5 grams of the sample should then be removed and placed in a sample cup for FPXRF analysis. The rest of the prepared sample should be sent off site for ICP or AA analysis. The method use for confirmatory analysis should meet the data quality objectives of the project.

7.3 Blank Samples: The blank samples should be from a "clean" quartz or silicon dioxide matrix that is free of any analytes at concentrations above the method detection limits. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

7.4 Standard Reference Materials: Standard reference materials (SRM) are standards containing certified amounts of metals in soil or sediment. These standards are used for accuracy and performance checks of FPXRF analyses. SRMs can be obtained from the National Institute of Standards and Technology (NIST), the U.S. Geological Survey (USGS), the Canadian National Research Council, and the national bureau of standards in foreign nations. Pertinent NIST SRMs for FPXRF analysis include 2704, Buffalo River Sediment; 2709, San Joaquin Soil; and 2710 and 2711, Montana Soil. These SRMs contain soil or sediment from actual sites that has been analyzed using independent inorganic analytical methods by many different laboratories.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample handling and preservation procedures used in FPXRF analyses should follow the guidelines in Chapter Three, Inorganic Analytes.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance protocols. All field data sheets and quality control data should be maintained for reference or inspection.

9.2 Energy Calibration Check: To determine whether an FPXRF instrument is operating within resolution and stability tolerances, an energy calibration check should be run. The energy calibration check determines whether the characteristic x-ray lines are shifting, which would indicate drift within the instrument. As discussed in Section 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (> 10 to 20 E F). The energy calibration check should be run at a frequency consistent with manufacturers recommendations. Generally, this would be at the beginning of each working day, after the batteries are changed or the instrument is shut off, at the end of each working day, and at any other time when the instrument operator believes that drift is occurring during analysis. A pure element such as iron, manganese, copper, or lead is often used for the energy calibration check. A manufacturer-recommended count time per source should be used for the check.

9.2.1 The instrument manufacturer's manual specifies the channel or kiloelectron volt level at which a pure element peak should appear and the expected intensity of the peak. The intensity and channel number of the pure element as measured

using the radioactive source should be checked and compared to the manufacturer's recommendation. If the energy calibration check does not meet the manufacturer's criteria, then the pure element sample should be repositioned and reanalyzed. If the criteria are still not met, then an energy calibration should be performed as described in the manufacturer's manual. With some FPXRF instruments, once a spectrum is acquired from the energy calibration check, the peak can be optimized and realigned to the manufacturer's specifications using their software.

9.3 Blank Samples: Two types of blank samples should be analyzed for FPXRF analysis: instrument blanks and method blanks. An instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window.

9.3.1 The instrument blank can be silicon dioxide, a Teflon block, a quartz block, "clean" sand, or lithium carbonate. This instrument blank should be analyzed on each working day before and after analyses are conducted and once per every twenty samples. An instrument blank should also be analyzed whenever contamination is suspected by the analyst. The frequency of analysis will vary with the data quality objectives of the project. A manufacturer-recommended count time per source should be used for the blank analysis. No element concentrations above the method detection limits should be found in the instrument blank. If concentrations exceed these limits, then the probe window and the check sample should be checked for contamination. If contamination is not a problem, then the instrument must be "zeroed" by following the manufacturer's instructions.

9.3.2 A method blank is used to monitor for laboratory-induced contaminants or interferences. The method blank can be "clean" silica sand or lithium carbonate that undergoes the same preparation procedure as the samples. A method blank must be analyzed at least daily. The frequency of analysis will depend on the data quality objectives of the project. To be acceptable, a method blank must not contain any analyte at a concentration above its method detection limit. If an analyte's concentration exceeds its method detection limit, the cause of the problem must be identified, and all samples analyzed with the method blank must be reanalyzed.

9.4 Calibration Verification Checks: A calibration verification check sample is used to check the accuracy of the instrument and to assess the stability and consistency of the analysis for the analytes of interest. A check sample should be analyzed at the beginning of each working day, during active sample analyses, and at the end of each working day. The frequency of calibration checks during active analysis will depend on the data quality objectives of the project. The check sample should be a well characterized soil sample from the site that is representative of site samples in terms of particle size and degree of homogeneity and that contains contaminants at concentrations near the action levels. If a site-specific sample is not available, then an NIST or other SRM that contains the analytes of interest can be used to verify the accuracy of the instrument. The measured value for each target analyte should be within ± 20 percent (%D) of the true value for the calibration verification check to be acceptable. If a measured value falls outside this range, then the check sample should be reanalyzed. If the value continues to fall outside the acceptance range, the instrument should be recalibrated, and the batch of samples analyzed before the unacceptable calibration verification check must be reanalyzed.

9.5 Precision Measurements: The precision of the method is monitored by analyzing a sample with low, moderate, or high concentrations of target analytes. The frequency of precision measurements will depend on the data quality objectives for the data. A minimum of

one precision sample should be run per day. Each precision sample should be analyzed 7 times in replicate. It is recommended that precision measurements be obtained for samples with varying concentration ranges to assess the effect of concentration on method precision. Determining method precision for analytes at concentrations near the site action levels can be extremely important if the FPXRF results are to be used in an enforcement action; therefore, selection of at least one sample with target analyte concentrations at or near the site action levels or levels of concern is recommended. A precision sample is analyzed by the instrument for the same field analysis time as used for other project samples. The relative standard deviation (RSD) of the sample mean is used to assess method precision. For FPXRF data to be considered adequately precise, the RSD should not be greater than 20 percent with the exception of chromium. RSD values for chromium should not be greater than 30 percent.

The equation for calculating RSD is as follows:

$$\text{RSD} = (\text{SD}/\text{Mean Concentration}) \times 100$$

where:

RSD = Relative standard deviation for the precision measurement for the analyte

SD = Standard deviation of the concentration for the analyte

Mean Concentration = Mean concentration for the analyte

The precision or reproducibility of a measurement will improve with increasing count time, however, increasing the count time by a factor of 4 will provide only 2 times better precision, so there is a point of diminishing return. Increasing the count time also improves the detection limit, but decreases sample throughput.

9.6 Detection Limits: Results for replicate analyses of a low-concentration sample, SSCS, or SRM can be used to generate an average site-specific method detection and quantitation limits. In this case, the method detection limit is defined as 3 times the standard deviation of the results for the low-concentration samples and the method quantitation limit is defined as 10 times the standard deviation of the same results. Another means of determining method detection and quantitation limits involves use of counting statistics. In FPXRF analysis, the standard deviation from counting statistics is defined as $\text{SD} = (N)^{1/2}$, where SD is the standard deviation for a target analyte peak and N is the net counts for the peak of the analyte of interest (i.e., gross counts minus background under the peak). Three times this standard deviation would be the method detection limit and 10 times this standard deviation would be the method quantitation limit. If both of the above mentioned approaches are used to calculate method detection limits, the larger of the standard deviations should be used to provide the more conservative detection limits.

This SD based detection limit criteria must be used by the operator to evaluate each measurement for its useability. A measurement above the average calculated or manufacturer's detection limit, but smaller than three times its associated SD, should not be used as a quantitative measurement. Conversely, if the measurement is below the average calculated or manufacturer's detection limit, but greater than three times its associated SD. It should be coded as an estimated value.

9.7 Confirmatory Samples: The comparability of the FPXRF analysis is determined by submitting FPXRF-analyzed samples for analysis at a laboratory. The method of confirmatory analysis must meet the project and XRF measurement data quality objectives. The confirmatory

samples must be splits of the well homogenized sample material. In some cases the prepared sample cups can be submitted. A minimum of 1 sample for each 20 FPXRF-analyzed samples should be submitted for confirmatory analysis. This frequency will depend on data quality objectives. The confirmatory analyses can also be used to verify the quality of the FPXRF data. The confirmatory samples should be selected from the lower, middle, and upper range of concentrations measured by the FPXRF. They should also include samples with analyte concentrations at or near the site action levels. The results of the confirmatory analysis and FPXRF analyses should be evaluated with a least squares linear regression analysis. If the measured concentrations span more than one order of magnitude, the data should be log-transformed to standardize variance which is proportional to the magnitude of measurement. The correlation coefficient (r^2) for the results should be 0.7 or greater for the FPXRF data to be considered screening level data. If the r^2 is 0.9 or greater and inferential statistics indicate the FPXRF data and the confirmatory data are statistically equivalent at a 99 percent confidence level, the data could potentially meet definitive level data criteria.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument Calibration: Instrument calibration procedures vary among FPXRF instruments. Users of this method should follow the calibration procedures outlined in the operator's manual for each specific FPXRF instrument. Generally, however, three types of calibration procedures exist for FPXRF instruments: FP calibration, empirical calibration, and the Compton peak ratio or normalization method. These three types of calibration are discussed below.

10.2 Fundamental Parameters Calibration: FP calibration procedures are extremely variable. An FP calibration provides the analyst with a "standardless" calibration. The advantages of FP calibrations over empirical calibrations include the following:

- No previously collected site-specific samples are required, although site-specific samples with confirmed and validated analytical results for all elements present could be used.
- Cost is reduced because fewer confirmatory laboratory results or calibration standards are required.

However, the analyst should be aware of the limitations imposed on FP calibration by particle size and matrix effects. These limitations can be minimized by adhering to the preparation procedure described in Section 7.2. The two FP calibration processes discussed below are based on an effective energy FP routine and a back scatter with FP (BFP) routine. Each FPXRF FP calibration process is based on a different iterative algorithmic method. The calibration procedure for each routine is explained in detail in the manufacturer's user manual for each FPXRF instrument; in addition, training courses are offered for each instrument.

10.2.1 Effective Energy FP Calibration: The effective energy FP calibration is performed by the manufacturer before an instrument is sent to the analyst. Although SSCS can be used, the calibration relies on pure element standards or SRMs such as those obtained from NIST for the FP calibration. The effective energy routine relies on the spectrometer response to pure elements and FP iterative algorithms to compensate for various matrix effects.

Alpha coefficients are calculated using a variation of the Sherman equation, which calculates theoretical intensities from the measurement of pure element samples. These coefficients indicate the quantitative effect of each matrix element on an analyte's measured x-ray intensity. Next, the Lachance Traill algorithm is solved as a set of simultaneous equations based on the theoretical intensities. The alpha coefficients are then downloaded into the specific instrument.

The working effective energy FP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of sampling. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. A manufacturer-recommended count time per source should be used for the calibration check. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A percent difference (%D) is then calculated for each target analyte. The %D should be within ± 20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line or the y-intercept value for the analyte. The SRM or SSCS is reanalyzed until the %D falls within ± 20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

The equation to calibrate %D is as follows:

$$\%D = ((C_s - C_k) / C_k) \times 100$$

where:

%D = Percent difference

C_k = Certified concentration of standard sample

C_s = Measured concentration of standard sample

10.2.2 BFP Calibration: BFP calibration relies on the ability of the liquid nitrogen-cooled, Si(Li) solid-state detector to separate the coherent (Compton) and incoherent (Rayleigh) backscatter peaks of primary radiation. These peak intensities are known to be a function of sample composition, and the ratio of the Compton to Rayleigh peak is a function of the mass absorption of the sample. The calibration procedure is explained in detail in the instrument manufacturer's manual. Following is a general description of the BFP calibration procedure.

The concentrations of all detected and quantified elements are entered into the computer software system. Certified element results for an NIST SRM or confirmed and validated results for an SSCS can be used. In addition, the concentrations of oxygen and silicon must be entered; these two concentrations are not found in standard metals analyses. The manufacturer provides silicon and oxygen concentrations for typical soil types. Pure element standards are then analyzed using a manufacturer-recommended count time per source. The results are used to calculate correction factors in order to adjust for spectrum overlap of elements.

The working BFP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of the analysis. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. The standard sample is analyzed using a manufacturer-recommended count time per source to check the calibration curve. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A %D is then calculated for each target analyte. The %D should fall within ± 20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line the y-intercept value for the analyte. The standard sample is reanalyzed until the %D falls within ± 20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

10.3 Empirical Calibration: An empirical calibration can be performed with SSCS, site-typical standards, or standards prepared from metal oxides. A discussion of SSCS is included in Section 7.2; if no previously characterized samples exist for a specific site, site-typical standards can be used. Site-typical standards may be selected from commercially available characterized soils or from SSCS prepared for another site. The site-typical standards should closely approximate the site's soil matrix with respect to particle size distribution, mineralogy, and contaminant analytes. If neither SSCS nor site-typical standards are available, it is possible to make gravimetric standards by adding metal oxides to a "clean" sand or silicon dioxide matrix that simulates soil. Metal oxides can be purchased from various chemical vendors. If standards are made on site, a balance capable of weighing items to at least two decimal places is required. Concentrated ICP or AA standard solutions can also be used to make standards. These solutions are available in concentrations of 10,000 parts per million, thus only small volumes have to be added to the soil.

An empirical calibration using SSCS involves analysis of SSCS by the FPXRF instrument and by a conventional analytical method such as ICP or AA. A total acid digestion procedure should be used by the laboratory for sample preparation. Generally, a minimum of 10 and a maximum of 30 well characterized SSCS, site-typical standards, or prepared metal oxide standards are required to perform an adequate empirical calibration. The number of required standards depends on the number of analytes of interest and interfering elements. Theoretically, an empirical calibration with SSCS should provide the most accurate data for a site because the calibration compensates for site-specific matrix effects.

The first step in an empirical calibration is to analyze the pure element standards for the elements of interest. This enables the instrument to set channel limits for each element for spectral deconvolution. Next the SSCS, site-typical standards, or prepared metal oxide standards are analyzed using a count time of 200 seconds per source or a count time recommended by the manufacturer. This will produce a spectrum and net intensity of each analyte in each standard. The analyte concentrations for each standard are then entered into the instrument software; these concentrations are those obtained from the laboratory, the certified results, or the gravimetrically determined concentrations of the prepared standards. This gives the instrument analyte values to regress against corresponding intensities during the modeling stage. The regression equation correlates the concentrations of an analyte with its net intensity.

The calibration equation is developed using a least squares fit regression analysis. After the regression terms to be used in the equation are defined, a mathematical equation can be developed to calculate the analyte concentration in an unknown sample. In some FPXRF instruments, the software of the instrument calculates the regression equation. The software uses calculated intercept and slope values to form a multiterm equation. In conjunction with the software in the instrument, the operator can adjust the multiterm equation to minimize interelement interferences and optimize the intensity calibration curve.

It is possible to define up to six linear or nonlinear terms in the regression equation. Terms can be added and deleted to optimize the equation. The goal is to produce an equation with the smallest regression error and the highest correlation coefficient. These values are automatically computed by the software as the regression terms are added, deleted, or modified. It is also possible to delete data points from the regression line if these points are significant outliers or if they are heavily weighing the data. Once the regression equation has been selected for an analyte, the equation can be entered into the software for quantitation of analytes in subsequent samples. For an empirical calibration to be acceptable, the regression equation for a specific analyte should have a correlation coefficient of 0.98 or greater or meet the DQOs of the project.

In an empirical calibration, one must apply the DQOs of the project and ascertain critical or action levels for the analytes of interest. It is within these concentration ranges or around these action levels that the FPXRF instrument should be calibrated most accurately. It may not be possible to develop a good regression equation over several orders of analyte concentration.

10.4 Compton Normalization Method: The Compton normalization method is based on analysis of a single, certified standard and normalization for the Compton peak. The Compton peak is produced from incoherent backscattering of x-ray radiation from the excitation source and is present in the spectrum of every sample. The Compton peak intensity changes with differing matrices. Generally, matrices dominated by lighter elements produce a larger Compton peak, and those dominated by heavier elements produce a smaller Compton peak. Normalizing to the Compton peak can reduce problems with varying matrix effects among samples. Compton normalization is similar to the use of internal standards in organics analysis. The Compton normalization method may not be effective when analyte concentrations exceed a few percent.

The certified standard used for this type of calibration could be an NIST SRM such as 2710 or 2711. The SRM must be a matrix similar to the samples and must contain the analytes of interests at concentrations near those expected in the samples. First, a response factor has to be determined for each analyte. This factor is calculated by dividing the net peak intensity by the analyte concentration. The net peak intensity is gross intensity corrected for baseline interference. Concentrations of analytes in samples are then determined by multiplying the baseline corrected analyte signal intensity by the normalization factor and by the response factor. The normalization factor is the quotient of the baseline corrected Compton K_{α} peak intensity of the SRM divided by that of the samples. Depending on the FPXRF instrument used, these calculations may be done manually or by the instrument software.

11.0 PROCEDURE

11.1 Operation of the various FPXRF instruments will vary according to the manufacturers' protocols. Before operating any FPXRF instrument, one should consult the manufacturer's manual. Most manufacturers recommend that their instruments be allowed to warm up for 15 to 30 minutes before analysis of samples. This will help alleviate drift or energy calibration problems later on in analysis.

11.2 Each FPXRF instrument should be operated according to the manufacturer's recommendations. There are two modes in which FPXRF instruments can be operated: in situ and intrusive. The in situ mode involves analysis of an undisturbed soil sediment or sample. Intrusive analysis involves collection and preparation of a soil or sediment sample before analysis. Some FPXRF instruments can operate in both modes of analysis, while others are designed to operate in only one mode. The two modes of analysis are discussed below.

11.3 For in situ analysis, one requirement is that any large or nonrepresentative debris be removed from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Another requirement is that the soil surface be as smooth as possible so that the probe window will have good contact with the surface. This may require some leveling of the surface with a stainless-steel trowel. During the study conducted to provide data for this method, this modest amount of sample preparation was found to take less than 5 minutes per sample location. The last requirement is that the soil or sediment not be saturated with water. Manufacturers state that their FPXRF instruments will perform adequately for soils with moisture contents of 5 to 20 percent but will not perform well for saturated soils, especially if ponded water exists on the surface. Another recommended technique for *in situ* analysis is to tamp the soil to increase soil density and compactness for better repeatability and representativeness. This condition is especially important for heavy element analysis, such as barium. Source count times for in situ analysis usually range from 30 to 120 seconds, but source count times will vary among instruments and depending on required detection limits.

11.4 For intrusive analysis of surface or sediment, it is recommended that a sample be collected from a 4- by 4-inch square that is 1 inch deep. This will produce a soil sample of approximately 375 grams or 250 cm³, which is enough soil to fill an 8-ounce jar. The sample should be homogenized, dried, and ground before analysis. The sample can be homogenized before or after drying. The homogenization technique to be used after drying is discussed in Section 4.2. If the sample is homogenized before drying, it should be thoroughly mixed in a beaker or similar container, or if the sample is moist and has a high clay content, it can be kneaded in a plastic bag. One way to monitor homogenization when the sample is kneaded in a plastic bag is to add sodium fluorescein dye to the sample. After the moist sample has been homogenized, it is examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly distributed in the sample, homogenization is considered complete; if the dye is not evenly distributed, mixing should continue until the sample has been thoroughly homogenized. During the study conducted to provide data for this method, the homogenization procedure using the fluorescein dye required 3 to 5 minutes per sample. As demonstrated in Sections 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, it can be used without the more labor intensive steps of drying, grinding, and sieving given in Sections 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps must be followed.

11.5 Once the soil or sediment sample has been homogenized, it should be dried. This can be accomplished with a toaster oven or convection oven. A small aliquot of the sample (20 to 50 grams) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hours in the convection or toaster oven at a temperature not greater than 150 E C. Microwave drying is not a recommended procedure. Field studies have shown that microwave drying can increase variability between the FPXRF data and confirmatory analysis. High levels of metals in a sample can cause arcing in the microwave oven, and sometimes slag forms in the sample. Microwave oven drying can also melt plastic containers used to hold the sample.

11.6 The homogenized dried sample material should be ground with a mortar and pestle and passed through a 60-mesh sieve to achieve a uniform particle size. Sample grinding should continue until at least 90 percent of the original sample passes through the sieve. The grinding step normally takes an average of 10 minutes per sample. An aliquot of the sieved sample should then be placed in a 31.0-mm polyethylene sample cup (or equivalent) for analysis. The sample cup should be one-half to three-quarters full at a minimum. The sample cup should be covered with a 2.5 μm Mylar (or equivalent) film for analysis. The rest of the soil sample should be placed in a jar, labeled, and archived for possible confirmation analysis. All equipment including the mortar, pestle, and sieves must be thoroughly cleaned so that any cross-contamination is below the MDLs of the procedure or DQOs of the analysis.

12.0 DATA ANALYSIS AND CALCULATIONS

Most FPXRF instruments have software capable of storing all analytical results and spectra. The results are displayed in parts per million and can be downloaded to a PC, which can provide a hard copy printout. Individual measurements that are smaller than three times their associated SD should not be used for quantitation.

13.0 METHOD PERFORMANCE

13.1 This section discusses four performance factors, field-based method detection limits, precision, accuracy, and comparability to EPA-approved methods. The numbers presented in Tables 4 through 9 were generated from data obtained from six FPXRF instruments. The soil samples analyzed by the six FPXRF instruments were collected from two sites in the United States. The soil samples contained several of the target analytes at concentrations ranging from nondetect to tens of thousands of mg/kg.

13.2 The six FPXRF instruments included the TN 9000 and TN Lead Analyzer manufactured by TN Spectrace; the X-MET 920 with a SiLi detector and X-MET 920 with a gas-filled proportional detector manufactured by Metorex, Inc.; the XL Spectrum Analyzer manufactured by Niton; and the MAP Spectrum Analyzer manufactured by Scitec. The TN 9000 and TN Lead Analyzer both have a HgI2 detector. The TN 9000 utilized an Fe-55, Cd-109, and Am-241 source. The TN Lead Analyzer had only a Cd-109 source. The X-Met 920 with the SiLi detector had a Cd-109 and Am-241 source. The X-MET 920 with the gas-filled proportional detector had only a Cd-109 source. The XL Spectrum Analyzer utilized a silicon pin-diode detector and a Cd-109 source. The MAP Spectrum Analyzer utilized a solid-state silicon detector and a Cd-109 source.

13.3 All data presented in Tables 4 through 9 were generated using the following calibrations and source count times. The TN 9000 and TN Lead Analyzer were calibrated using fundamental parameters using NIST SRM 2710 as a calibration check sample. The TN 9000 was operated using 100, 60, and 60 second count times for the Cd-109, Fe-55, and Am-241 sources, respectively. The TN Lead analyzer was operated using a 60 second count time for the Cd-109 source. The X-MET 920 with the Si(Li) detector was calibrated using fundamental parameters and one well characterized site-specific soil standard as a calibration check. It used 140 and 100 second count times for the Cd-109 and Am-241 sources, respectively. The X-MET 920 with the gas-filled proportional detector was calibrated empirically using between 10 and 20 well characterized site-specific soil standards. It used 120 second times for the Cd-109 source. The XL Spectrum Analyzer utilized NIST SRM 2710 for calibration and the Compton peak normalization procedure for quantitation based on 60 second count times for the Cd-109 source.

The MAP Spectrum Analyzer was internally calibrated by the manufacturer. The calibration was checked using a well-characterized site-specific soil standard. It used 240 second times for the Cd-109 source.

13.4 Field-Based Method Detection Limits: The field-based method detection limits are presented in Table 4. The field-based method detection limits were determined by collecting ten replicate measurements on site-specific soil samples with metals concentrations 2 to 5 times the expected method detection limits. Based on these ten replicate measurements, a standard deviation on the replicate analysis was calculated. The method detection limits presented in Table 4 are defined as 3 times the standard deviation for each analyte.

The field-based method detection limits were generated by using the count times discussed earlier in this section. All the field-based method detection limits were calculated for soil samples that had been dried and ground and placed in a sample cup with the exception of the MAP Spectrum Analyzer. This instrument can only be operated in the *in situ* mode, meaning the samples were moist and not ground.

Some of the analytes such as cadmium, mercury, silver, selenium, and thorium were not detected or only detected at very low concentrations such that a field-based method detection limit could not be determined. These analytes are not presented in Table 4. Other analytes such as calcium, iron, potassium, and titanium were only found at high concentrations (thousands of mg/kg) so that reasonable method detection limits could not be calculated. These analytes also are not presented in Table 4.

13.5 Precision Measurements: The precision data is presented in Table 5. Each of the six FPXRF instruments performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from nondetects to thousands of mg/kg. Each of the 12 soil samples underwent 4 different preparation techniques from *in situ* (no preparation) to dried and ground in a sample cup. Therefore, there were 48 precision data points for five of the instruments and 24 precision points for the MAP Spectrum Analyzer. The replicate measurements were taken using the source count times discussed at the beginning of this section.

For each detectable analyte in each precision sample a mean concentration, standard deviation, and RSD was calculated for each analyte. The data presented in Table 5 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the MDL for that analyte for each instrument. Some analytes such as mercury, selenium, silver, and thorium were not detected in any of the precision samples so these analytes are not listed in Table 5. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the MDLs so that an RSD value calculated at 5 to 10 times the MDL was not possible.

One FPXRF instrument collected replicate measurements on an additional nine soil samples to provide a better assessment of the effect of sample preparation on precision. Table 6 shows these results. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the detection limit of the FPXRF analyzer to thousands of mg/kg. The FPXRF analyzer only collected replicate measurements from three of the preparation methods; no measurements were collected from the *in situ* homogenized samples. The FPXRF analyzer conducted five replicate measurements of the *in situ* field samples by taking measurements at five different points within the 4-inch by 4-inch sample square. Ten replicate measurements were collected for both the intrusive undried and unground and intrusive dried and ground samples contained in cups. The cups were shaken between each replicate measurement.

Table 6 shows that the precision dramatically improved from the in situ to the intrusive measurements. In general there was a slight improvement in precision when the sample was dried and ground. Two factors caused the precision for the in situ measurements to be poorer. The major factor is soil heterogeneity. By moving the probe within the 4-inch by 4-inch square, measurements of different soil samples were actually taking place within the square. Table 6 illustrates the dominant effect of soil heterogeneity. It overwhelmed instrument precision when the FPXRF analyzer was used in this mode. The second factor that caused the RSD values to be higher for the in situ measurements is the fact that only five versus ten replicates were taken. A lesser number of measurements caused the standard deviation to be larger which in turn elevated the RSD values.

13.6 Accuracy Measurements: Five of the FPXRF instruments (not including the MAP Spectrum Analyzer) analyzed 18 SRMs using the source count times and calibration methods given at the beginning of this section. The 18 SRMs included 9 soil SRMs, 4 stream or river sediment SRMs, 2 sludge SRMs, and 3 ash SRMs. Each of the SRMs contained known concentrations of certain target analytes. A percent recovery was calculated for each analyte in each SRM for each FPXRF instrument. Table 7 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 7 were generated from the 13 soil and sediment SRMs only. The 2 sludge and 3 ash SRMs were included for cadmium, chromium, and nickel because of the low or nondetectable concentrations of these three analytes in the soil and sediment SRMs.

Only 12 analytes are presented in Table 7. These are the analytes that are of environmental concern and provided a significant number of detections in the SRMs for an accuracy assessment. No data is presented for the X-MET 920 with the gas-filled proportional detector. This FPXRF instrument was calibrated empirically using site-specific soil samples. The percent recovery values from this instrument were very sporadic and the data did not lend itself to presentation in Table 7.

Table 8 provides a more detailed summary of accuracy data for one FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. Table 8 shows the certified value, measured value, and percent recovery for five analytes. These analytes were chosen because they are of environmental concern and were most prevalently certified for in the SRM and detected by the FPXRF instrument. The first nine SRMs are soil and the last 4 SRMs are sediment. Percent recoveries for the four NIST SRMs were often between 90 and 110 percent for all analytes.

13.7 Comparability: Comparability refers to the confidence with which one data set can be compared to another. In this case, FPXRF data generated from a large study of six FPXRF instruments was compared to SW-846 Methods 3050 and 6010 which are the standard soil extraction for metals and analysis by inductively coupled plasma. An evaluation of comparability was conducted by using linear regression analysis. Three factors were determined using the linear regression. These factors were the y-intercept, the slope of the line, and the coefficient of determination (r^2).

As part of the comparability assessment, the effects of soil type and preparation methods were studied. Three soil types (textures) and four preparation methods were examined during the study. The preparation methods evaluated the cumulative effect of particle size, moisture, and homogenization on comparability. Due to the large volume of data produced during this study, linear regression data for six analytes from only one FPXRF instrument is presented in Table 9. Similar trends in the data were seen for all instruments.

Table 9 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. The soil types are as follows: soil 1--sand; soil 2--loam; and soil 3--silty clay. The preparation methods are as follows: preparation 1--in situ in the field; preparation 2--in situ, sample collected and homogenized; preparation 3--intrusive, with sample in a sample cup but sample still wet and not ground; and preparation 4--sample dried, ground, passed through a 40-mesh sieve, and placed in sample cup.

For arsenic, copper, lead, and zinc, the comparability to the confirmatory laboratory was excellent with r^2 values ranging from 0.80 to 0.99 for all six FPXRF instruments. The slopes of the regression lines for arsenic, copper, lead, and zinc, were generally between 0.90 and 1.00 indicating the data would need to be corrected very little or not at all to match the confirmatory laboratory data. The r^2 values and slopes of the regression lines for barium and chromium were not as good as for the other for analytes, indicating the data would have to be corrected to match the confirmatory laboratory.

Table 9 demonstrates that there was little effect of soil type on the regression parameters for any of the six analytes. The only exceptions were for barium in soil 1 and copper in soil 3. In both of these cases, however, it is actually a concentration effect and not a soil effect causing the poorer comparability. All barium and copper concentrations in soil 1 and 3, respectively, were less than 350 mg/kg.

Table 9 shows there was a preparation effect on the regression parameters for all six analytes. With the exception of chromium, the regression parameters were primarily improved going from preparation 1 to preparation 2. In this step, the sample was removed from the soil surface, all large debris was removed, and the sample was thoroughly homogenized. The additional two preparation methods did little to improve the regression parameters. This data indicates that homogenization is the most critical factor when comparing the results. It is essential that the sample sent to the confirmatory laboratory match the FPXRF sample as closely as possible.

Section 11.0 of this method discusses the time necessary for each of the sample preparation techniques. Based on the data quality objectives for the project, an analyst must decide if it is worth the extra time required to dry and grind the sample for small improvements in comparability. Homogenization requires 3 to 5 minutes. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 minutes per sample. Lastly, when grinding and sieving is conducted, time must be allotted to decontaminate the mortars, pestles, and sieves. Drying and grinding the samples and decontamination procedures will often dictate that an extra person be on site so that the analyst can keep up with the sample collection crew. The cost of requiring an extra person on site to prepare samples must be balanced with the gain in data quality and sample throughput.

13.8 The following documents may provide additional guidance and insight on this method and technique:

13.8.1 Hewitt, A.D. 1994. "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton K_{α} Peak Normalization Analysis." *American Environmental Laboratory*. Pages 24-32.

13.8.2 Piorek, S., and J.R. Pasmore. 1993. "Standardless, In Situ Analysis of Metallic Contaminants in the Natural Environment With a PC-Based, High Resolution Portable X-Ray Analyzer." *Third International Symposium on Field Screening Methods*

for Hazardous Waste and Toxic Chemicals. Las Vegas, Nevada. February 24-26, 1993. Volume 2, Pages 1135-1151.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Metorex. X-MET 920 User's Manual.
2. Spectrace Instruments. 1994. Energy Dispersive X-ray Fluorescence Spectrometry: An Introduction.
3. TN Spectrace. Spectrace 9000 Field Portable/Benchtop XRF Training and Applications Manual.
4. Unpublished SITE data, received from PRC Environment Management, Inc.

APPENDIX C

YEAR OF CONSTRUCTION AND SOIL LEAD LEVELS FOR SAMPLES

<u>Sample</u>	<u>Year of Construction</u>	<u>Exterior Composition</u>	<u>Soil Lead Levels (ppm)</u>
A1	1889	Frame	15,100 ± 330
A2	1894	Frame	5610 ± 140
A3	1890	Frame	7490 ± 18
A4	ND*	Frame	27,000 ± 570
A5	1890	Frame	776 ± 51
A6	1874	Frame	817 ± 48
A7	1906	Other	207 ± 35
A8	1896	Brick	< 41.0
A9	1924	Brick	250 ± 36
A10	1907	Brick	1120 ± 58
A11	1890	Brick	2890 ± 95
A12	1890	Other	324 ± 38
A13	1920	Other	1280 ± 62
A14	1905	Brick	1280 ± 60
A15	1937	Other	430 ± 41
A16	1890	Other	6140 ± 160
A17	1851	Brick	367 ± 39
A18	1914	Brick	367 ± 40
A19	1930	Brick	91.6 ± 31
A20	1880	Brick	3880 ± 120
A21	1895	Brick	11,700 ± 260
A22	1882	Brick	< 44.0
A23	1885	Other	< 45.0
A24	1870	Other	299 ± 37
A25	1843	Brick	416 ± 40
A26	ND*	Other	478 ± 41
A27	1914	Brick	9310 ± 210
A28	1918	Other	269 ± 36
A29	1895	Frame	2300 ± 83
A30	1910	Frame	114 ± 29

* ND= No date

Other housing units included: brick/frame combination (2), aluminum/vinyl siding (6), and rock (1).